LABORATORY NOTES

ON

IRON AND STEEL ANALYSES

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BY

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PREFACE.

THESE notes were in the first instance written for the guidance of the staff in an iron and steel works laboratory, which was for some years under the supervision of the author, and where the results of over 40,000 estimations were annually placed on record.

The methods required to be reliable and rapid so as to control and keep pace with the manufacturing operations. It was necessary that all the analysts should work on identical lines. By estimations made at intervals on standard substances, uniform results were regularly obtained from all the members of the staff in the laboratory. The accuracy of the methods was tested in daily practice, and confirmed by analysts acting on behalf of buyers and sellers at home and on the Continent.

The notes have been kept up to date, and have been found useful in the metallurgical laboratory maintained by the County Committee and the Local Committee at the Wednesbury Metallurgical Centre. The high position gained by the Staffordshire students at the Honours Examinations conducted at the

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Royal College of Science, and the Imperial College of Science and Technology, London, further attest their usefulness.

In compliance with numerous and repeated requests the notes have been extended and are now published. In their present form it is hoped that they will have an enlarged sphere of usefulness for Metallurgical Students, for Engineers and Foundrymen (who in increasing numbers desire to have an acquaintance with analytical methods), for Iron and Steel Works' Chemists, and for Public Analysts.

The general aim of the book has been to set out the complete course of an assay or an analysis in full detail. In many cases whole paragraphs have been reintroduced, where necessary, to obviate the confusion arising from cross references.

The analytical methods are given in detail, precise quantities are stated, and the most convenient sizes of beakers, &c., are specified. In these there is no intention of imperiousness. Time and money can be saved by avoiding the waste due to the use of unnecessary excess of chemicals. Good results have been obtained in every-day practice by implicitly following the instructions embodied in the notes. But they must be followed thoughtfully : no book of directions can be a substitute for brains.

Examples of calculations are freely given throughout the notes, as these have been found to be helpful.

The preparation of the necessary solutions is dealt with in a separate part of the book. This arrangement has many advantages.

Permission to include valuable extracts has kindly been given by the Council of the Iron and Steel Institute (London), the Editor of the *Journal of the American Chemical Society*, the Editor of the *Chemical News*, the Editor of *Technics*, and Mr. J. M. Camp, Chairman of the United States Steel Corporation Chemists' Committee. Mr. W. H. Merritt, of the Royal School of Mines, London, has furnished notes of an important method. Former students— Messrs. J. H. Colley (Royal Spanish Arsenal), H. Essex (Hatherton), Percy Hill (Wednesbury), E. O. Howell (Round Oak), Samuel Lamb (Royal School of Mines), Gordon Mills (Nova Scotia Steel Works), and C. H. Rose (Frodingham)—have supplied some of the notes. Mr. A. C. Hoare has supplied some data, and has assisted in revising the proofs. To all these the author tenders his thanks.

THE MUNICIPAL SCIENCE SCHOOL,
    WEDNESBURY, *July*, 1909.

CONTENTS.

LIST OF ILLUSTRATIONS.

ATOMIC WEIGHTS

USED IN THIS BOOK.

	Chemical Symbol.	Atomic Weight.		Chemical Symbol.	Atomic Weight.
Aluminium,	Al	27·1	Molybdenum.	Mo	96·0
Arsenic, . .	As	75·0	Nickel, . .	Ni	58·7
Barium, . .	Ba	137·4	Nitrogen, .	N	14·04
Cadmium, .	Cd	112·4	Oxygen, . .	O	16·0
Calcium, .	Ca	40·1	Phosphorus,	P	31·0
Carbon, . .	C	12·0	Potassium, .	K	39·15
Chlorine, .	Cl	35·5	Silicon, . .	Si	28·4
Chromium, .	Cr	52·1	Silver, . .	Ag	107·9
Cobalt, . .	Co	59·0	Sodium, . .	Na	23·0
Copper, . .	Cu	63·6	Sulphur, .	S	32·06
Fluorine, .	F	19·0	Tantalum, .	Ta	181·0
Hydrogen, .	H	1·0	Titanium, .	Ti	48·10
Iodine, . .	I	127·0	Tungsten or		
Iron, . . .	Fe	55·9	Wolfram,	W	184·0
Magnesium,	Mg	24·36	Vanadium, .	V	51·2
Manganese,	Mn	55·0			

ATOMIC WEIGHTS, REVISED 1909.

Iodine, . . .	126·92	Silicon, . . .	28·3
Manganese, . .	54·92	Sulphur, . . .	32·07

LABORATORY NOTES

ON

IRON AND STEEL ANALYSES.

ANALYSIS OF STEEL.

ESTIMATION OF COMBINED CARBON.

EGGERTZ' COLORIMETRIC METHOD.

Outline of the Process.—This method is based on the fact that when iron which contains carbon in a certain state of combination is dissolved in dilute nitric acid, a yellow-coloured solution is obtained, and the depth of the colour is, within limits, in proportion to the amount of carbon present in that state of combination.

In practice a weighed quantity of a standard steel is dissolved, the solution diluted to a definite volume in a graduated Eggertz' tube, and mixed well. A like quantity of the sample to be tested is treated exactly in the same manner, and the solution is carefully diluted in a corresponding graduated tube till the solution shows the same depth of colour. A short calculation then gives the percentage.

1

Notes on the Process.

The standard steel ought to have a composition approximating to that of the sample.

Siemens steel should be tested against Siemens steel, basic Bessemer steel against basic Bessemer steel, &c.

The standard and the sample steels should preferably have undergone the same thermal and mechanical treatment.

The mechanical condition of the standard and the sample should not differ widely.

A steel containing a high percentage of carbon requires more acid than one which contains a low percentage of carbon. A high-carbon steel requires to be heated during solution longer than a low-carbon one. But, obviously, both standard and sample ought to be treated with an equal amount of acid, and be heated for the same length of time.

The graduated Eggertz' tubes should be capable of containing 20 c.c. They should be of clear glass, and the bore of each should be equal to others of the same set. Each Eggertz' tube should have a ground glass stopper, or be bent at the top (see p. 386).

The amount of cold solution should be between 3 and 8 c.c. This reservation is now ignored.

The amount of carbon found by the colour test

may differ from that found in the same piece of steel after reheating, annealing, or other treatment.

Certain metals, such as chromium, copper, and nickel, interfere with the accuracy of the colour test for carbon.

In works' practice, the percentage of carbon in a steel is, as a rule, approximately known before being handed in to the laboratory. A suitable standard can therefore be chosen. If, however, the percentage of carbon in the standard differs too much from that of the steel which is being tested, another standard steel should be taken and a fresh comparison made.

The quantity of steel and acid taken for a test should, in some degree, correspond to the percentage of carbon present.

Suitable quantities are :—

For very soft steel, such as is produced for electrical purposes, with carbon under 0·05 per cent., it is advisable to work on 0·3 gramme of the sample dissolved in 5 c.c. of 1·2 specific gravity nitric acid.

For ordinary mild steel, as supplied for structural purposes, with about 0·18 per cent. of carbon, 0·2 gramme may be weighed off and treated with 3·5 c.c. of 1·2 specific gravity nitric acid.

For medium steel—for rails, tyres, axles, &c., containing from about 0·3 to 0·6 per cent. of carbon— 0·1 gramme of steel and 2 c.c. of 1·2 specific gravity nitric acid may conveniently be used.

For tool steels, with carbons ranging from 0·75 to

1·5 per cent., 0·10 gramme of the steel dissolved in 5 c.c. of 1·2 specific gravity nitric acid are convenient quantities.

In every case the weighed-off standard and sample should be treated with a like quantity of acid, and under exactly similar conditions.
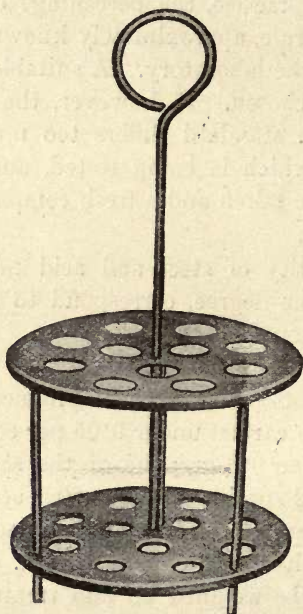
Fig. 1.—Rack for test tubes.

Details of the Process.—Weigh off a convenient quantity of a suitable standard steel, prepared as directed on pp. 11 and 12.

Transfer the weighed quantity to a 13 × 1·3 cm.

(about 5-inch × ½-inch) clean, dry test tube with a distinctive label or mark on it. A rubber ring makes a suitable distinction for the standard tube.

The test tube may be conveniently placed in the kind of rack shown in Fig. 1.

Weigh off a similar quantity of each sample of steel which is to be tested.

All drillings and turnings must be clean, and free from scale, oil, &c.

Transfer each weighed portion to a separate test tube, and note the sample number on each label.

To each weighed quantity measure the required volume of 1·2 specific gravity nitric acid.

When brisk action has ceased, set the test tube rack, with contents, in a bath of boiling water, and keep the bath at boiling point until all the steels are dissolved.

Take the test tube rack and contents from the hot bath, and set to cool in a dish of cold water.

When the solutions have cooled, proceed to compare the relative depths of colour.

The stand shown in Figs. 2 and 3 is useful. It provides a rack for the Eggertz' tubes, supports for the burette from which the acid is measured, support for the burette from which the water for dilution can be conveniently added, and a frame for carrying a light diffuser. A thin pane of ground glass may be fitted, or a piece of filter paper may be gummed on to the frame, or a pane of clear glass may be fitted, to which a piece of wet filter paper may be fastened—it will

easily be made to adhere—before making colour comparisons. A small cutting of rubber tubing is placed at the bottom of each tube recess to act as a pad. Over each burette an inverted test tube is placed to keep out dust.
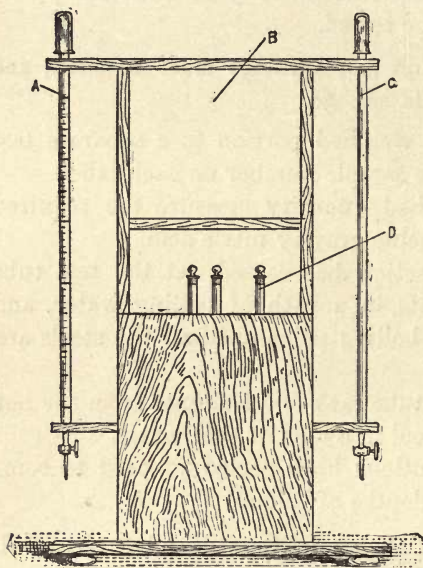
Fig. 2.—Stand for Eggertz' tubes— Front view.
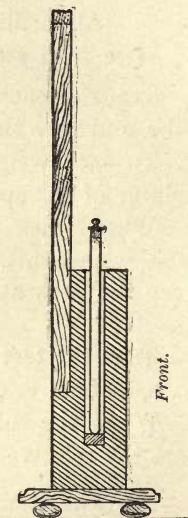
Fig. 3.—Stand for Eggertz' tubes— Cross section.

A, Burette for measuring acid.
B, Frame for light diffuser.
C, Burette for water.   D, Eggertz' tube.

To compare the coloured solutions, pour from the standard test tube into a graduated Eggertz' tube which has a distinguishing mark, such as a rubber

ring or a mark made with a diamond. With a fine jet of cold water rinse the test tube, and drain the rinsings into the graduated tube.

Make up to a definite measure with cold water.

Close the graduated tube, and shake it so as to thoroughly mix the fluids.

Transfer the solution from the other test tube to a corresponding Eggertz' tube. Rinse, drain, and mix as before.

Compare the depth of colour of the two solutions.

> NOTE.—In comparing the tints, the graduated tubes are placed side by side, so that diffused light coming through ground glass or a sheet of moistened filter paper will pass through the solutions. Change the relative positions of the tubes—standard tube to the right, and sample tube to the left, and *vice versâ*—during the comparison.

Dilute the darker coloured solution with cold water, mix well and compare again.

If necessary, dilute further, mix and compare. Repeat until the solution from the sample is of the same depth of tint as that of the standard.

Read off the volumes of the solutions, and calculate the result.

GENERAL RULE FOR CALCULATING.—Divide the percentage carbon of the standard steel by the volume of its solution, and multiply the result by the volume of the solution of the steel which is being tested.

EXAMPLE.—Standard steel contained 0·21 per cent. of carbon, and the solution was diluted to 6·3 c.c. The solution from the sample required to be diluted to 5·4 c.c.

Then $$\frac{0\cdot21}{6\cdot3} \times 5\cdot4 = 0\cdot18.$$

0·18 = percentage of carbon in the sample, as shown by the colour test.

It is usual to dilute the solution from the standard steel to such a volume that the percentage of carbon in the sample can be directly read off, or so that only a simple calculation is necessary.

EXAMPLE.—Standard steel contained 0·51 per cent of carbon, and the solution was diluted to 5·1 c.c.

The solution from the sample required to be diluted to 5·7 c.c.

∴ Percentage of carbon in the sample, as shown by the colour test = 0·57 per cent.

In the first example the solution from the standard steel was purposely diluted so that every 0·1 per cent. of carbon had 3 c.c. of liquid = 30 measures for each 1 per cent.—

$$\frac{6\cdot3}{30} = 0\cdot21.$$

Similarly, we divide the number of c.c. to which the solution from the sample was diluted—

$$\frac{5\cdot4}{30} = 0\cdot18.$$

0·18 = percentage of carbon in the sample.

Rapid Estimation of Carbon in Furnace Samples.

A sample of the "metal" is taken from the furnace in a "spoon," allowed to solidify, hammered, cooled, and drilled. The drillings are quickly tested by:—

Weighing off a suitable quantity of the drillings, dissolving in dilute nitric acid, using a small Bunsen burner to hasten the action of the acid, cooling under a water tap, transferring to an Eggertz' tube and comparing with a suitable standard. For very soft steels, it is not unusual to take 0·5 gramme of the drillings, and, having dissolved and cooled, diluting to about 20 c.c., and comparing in long Eggertz' tubes.

Estimation of Minute Quantities of Carbon.

J. E. Stead described[*] a new method for the estimation of minute quantities of carbon. This consists in adding solution of potash or soda to the nitric acid solution. The depth of colour is about two and a half times that of the acid solution.

The estimation is carried out thus: 1 gramme of the steel or iron to be tested is weighed off and placed in a 200 c.c. beaker, and, after covering with a watch-glass, 12 c.c. of nitric acid of 1·2 specific gravity are added. The beaker and contents are then placed on a warm plate, heated to about 90° to 100° C., and there allowed to remain until dissolved, which does not usually take more than ten minutes. At the

* *Journal of The Iron and Steel Institute*, No. 1, 1883, p. 213.

same time, a standard steel containing a known quantity of carbon is treated in exactly the same way, and when both are dissolved, 30 c.c. of hot water is added to each and 13 c.c. of standard solution of sodium hydrate of 1·27 specific gravity.

The contents are now to be well shaken, and then poured into a glass measuring-jar and diluted till they occupy a bulk of 60 c.c. After again well mixing and allowing to stand for ten minutes in a warm place, they are filtered through dry filters, and the filtrates, only a portion of which is used, are compared. This may be done by pouring the two liquids into two separate measuring tubes in such quantity or proportion that upon looking down the tubes the colours appear to be equal.

Thus if 50 mm. of the standard solution is poured into one tube, and if the steel to be tested contains, say, half as much as the standard, there will be 100 mm. of its colour solution required to give the same tint. The carbon is, therefore, inversely proportional to the bulk compared with the standard, and in the above assumed case if the standard steel contained 0·05 per cent. carbon, the following simple equation would give the carbon in the sample tested:—

$$\frac{0 \cdot 05 \times 50}{100} = 0 \cdot 025.$$

In the same interesting paper Stead describes a simple but efficient instrument for colour estimations.

For estimation of carbon by combustion see pp. 98 to 115.

Preparation of Standard Steel for Colour Test.

Procure a billet of steel of average composition and containing a suitable percentage of carbon. The steel selected must not have been overheated or subjected to any treatment having a tendency to alter the condition of the carbon—at least not more than superficially. On one side of the billet drill, with a broad drill, a series of holes of depth enough to permit the drill to more than clear a quarter of an inch below the surface.* Reject these drillings.

With a smaller drill continue for a short distance in, to drill a little from each of the holes. Collect these drillings. Drill a little more out of each hole and collect the drillings. If drilling is continued too long in any hole, the drillings become pulverised and worthless. The pulverising action increases with the depth of the hole, so that it is advisable to begin operations on another side of the billet rather than drill too deeply.

Care must be taken to keep oil and dust from the drillings.

When enough drillings have been collected, the finer portions and the rougher portions are separated by sifting, and are rejected. The remainder should

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* If more convenient the billet may be planed or turned rather than drilled, but all surface planings or turnings must be rejected.

be very well mixed and put away in a clean, dry, well-stoppered bottle; the stopper and neck being covered with india-rubber or parchment, and kept in a dry place. From that stock small quantities may be taken from time to time for daily use.

The percentage of carbon in the standard should be accurately ascertained by combustion (see method on p. 98), or should be compared with standards in use in good steel works and public laboratories.

ESTIMATION OF SILICON IN STEEL.

Outline of the Process.—When mild steel containing silicon is dissolved in hydrochloric acid, and the solution is evaporated to thorough dryness, the silicon becomes oxidised. On boiling the dried residue in hydrochloric acid, all the other components of ordinary mild steel are dissolved. The insoluble residue is collected on a filter, washed, dried, ignited, and weighed, and the percentage calculated.

If there is reason to suspect that the weighed residue is not pure silica (SiO_2), it may be fused with potassium bisulphate, washed, ignited, &c.

Details of the Process. — Weigh off 4·702 grammes of the sample.

Transfer the weighed portion to a 13 × 11·5 cm. (about 5-inch × 4½-inch) Jena or Bohemian * beaker.

Add 40 c.c. of hydrochloric acid of 1·16 specific gravity. This is of the specific gravity usually sold.

Evaporate on a hot plate to dryness. The residue should be well dried, but not "burnt" (see note on "hot plate," p. 377).

Withdraw the beaker and place it on a cork mat.

When the beaker is not likely to crack in contact

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* The size of beaker specified here and in other pages is not imperative. But it is more satisfactory to state a convenient size than to print "a medium-sized beaker."

with liquid, add 50 c.c. of hot water and 35 c.c. of hydrochloric acid of 1·16 specific gravity.

Boil for a few minutes to dissolve the **ferric** chloride, &c. Add about 80 c.c. of hot water.

Filter, using a 9 cm. Swedish filter.

Carefully remove the last granules of silica from the inside of the beaker on to the filter, using a "policeman" if necessary.

Wash the residue on the filter three or four times with dilute hydrochloric acid—1 of specific gravity 1·16 acid to 6 of water.

Wash several times with hot water.

All traces of colour should be removed from the filter paper and the precipitate. If washing does not effect this, the residue must be purified by fusion (see next page for details).

Fig 4.—Filter dryer.

If the residue is white, or of a grey tint on account of a little finely-divided graphite, dry it by placing the funnel with filter paper and contents on a filter dryer (Fig. 4), covering with paper, and allowing to dry on the hot plate.

Place the dried residue and filter paper in a tared platinum or porcelain crucible or capsule.

In a hot muffle furnace (Fig. 5) burn off the filter paper, and ignite for about half an hour.
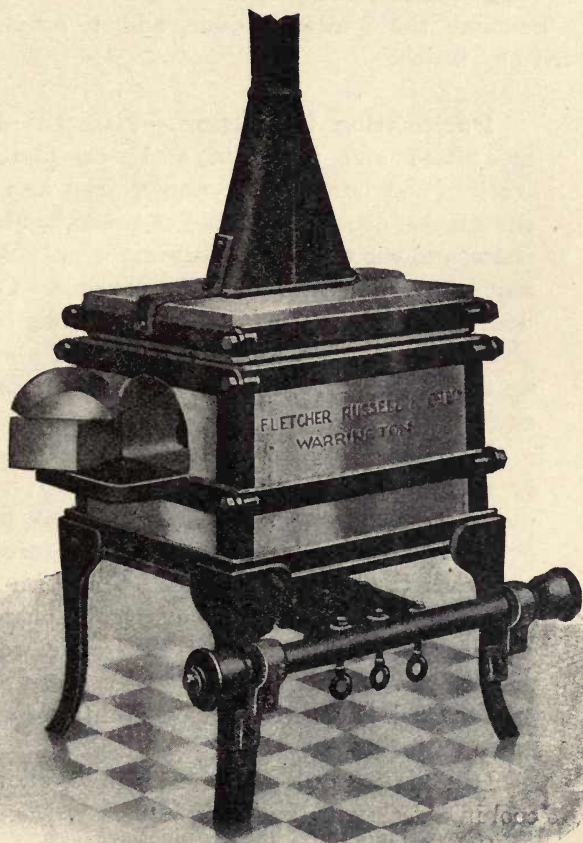
Fig. 5.—Muffle furnace.

Withdraw the crucible, &c., and allow to cool in a desiccator.

Weigh quickly, and note the weight.

Examine the ignited residue, and, if necessary, purify by fusion.

Purification by Fusion.—Place the dried precipitate and paper in a $1\frac{1}{2}$ - oz. platinum crucible, and burn off the paper. Put also into the crucible about 3 grammes of potassium bisulphate, and stir up with a platinum wire. Brush any adhering matter into the crucible. Cover with about $1\frac{1}{2}$ grammes more of potassium bisulphate, and fuse the whole, gently at first, keeping up the temperature as long as white fumes are evolved.

When the crucible has cooled a little, set it on its side in a deep porcelain basin, 5 inches diameter, and pour hot water into the basin. When the melt has loosened, take out the crucible and wash the contents into the basin. Stir well so as to dissolve as much of the sulphate as possible. Filter through a 12·5 cm. Swedish filter paper. Wash until all traces of sulphate are removed. Sometimes about 1 litre of water is required.

Dry the washed precipitate, ignite, allow to cool in a desiccator, and weigh quickly.

Calculate the percentage.

The ignited pure residue (SiO_2) contains 47·02 per cent. of silicon, and when 4·702 grammes of

sample are operated on, the factor for calculation is

$$\frac{47 \cdot 02}{4 \cdot 702} = 10.$$

EXAMPLE—   Grammes.

Weight of silica + ash + crucible				=	17·1354
„	crucible	.	.	=	17·1312
„	silica + ash	.	.	=	0·0042
„	ash .	.	.	=	0·0007
„	silica	.	.	=	0·0035

$0 \cdot 0035 \times 10 = 0 \cdot 035 =$ percentage of silicon in the sample.

If a quantity other than $4 \cdot 702$ grammes be taken for analysis, calculate thus—

$$\frac{\text{Weight of silica} \times 47 \cdot 02}{\text{Weight of sample taken}} = \text{percentage of silicon.}$$

Log $47 \cdot 02 = 1 \cdot 6722826.$

2

ESTIMATION OF PHOSPHORUS IN STEEL.

The Molybdate Method.

Outline of the Process.—The phosphorus in the weighed portion of the sample is oxidised to phosphoric acid, which can, in a properly regulated solution, form a precipitate, $[(NH_4)_3PO_4 . 12MoO_3]$, containing a definite percentage of phosphorus. The precipitate is collected, washed, dried, and weighed. From the weight of the precipitate the percentage of phosphorus in the steel is calculated.

In estimating phosphorus by this method, regard must be paid to the quantity, the degree of acidity, and the temperature of the solution when precipitating. The amount of ammonium nitrate in the solution has also an effect on the precipitation. If the weight of the precipitate exceeds 0·3 gramme its composition may be irregular.

Details of the Process.—For mild and medium steels which are free, or practically free, from arsenic.

Weigh off 2 grammes of the drillings.

Transfer the weighed portion to a 14 × 13 cm. (about 5½ × 5-inch) spouted Jena or Bohemian beaker. A wide beaker facilitates evaporation ; a tall beaker minimises risk of loss by spirting.

Add 20 c.c. of 1·42 specific gravity nitric acid along with 7 c.c. of water. Higher carbon steels require more acid.

Evaporate on a hot plate to dryness (see note on hot plate, p. 377). When, towards the end of the evaporation, there is much danger of loss by spirting, interpose a thin piece of wire gauze between the plate and the beaker. The evaporation will then proceed more quietly till finished.

Allow the beaker to remain on the hot plate for five minutes more, so as to oxidise all the phosphorus.

Withdraw the beaker and place it on a cork mat.

When the beaker is not likely to crack on contact with liquid, add 15 c.c. of 1·16 specific gravity hydrochloric acid.

Evaporate till the liquid is of the smallest possible bulk. If evaporation has been continued till some of the solution has dried on the glass, withdraw the beaker, and, when it has slightly cooled, gently pour one or more drops of hydrochloric acid on the spot, to dissolve the solidified matter. The beaker will then contain a concentrated and nearly neutral solution or syrup.

With a fine-spout wash-bottle containing warm water, wash the solution into a 150 c.c. (about 5-oz.) conical (Erlenmeyer) flask. Avoid dilution as much as possible. The solution and washings should not measure more than 15 c.c.

Add 17 c.c. of ammonium nitrate solution (see p. 402).

Heat to about 90° C.

Immediately raise the thermometer about 2·5 cm. (about 1 inch) clear of the solution, and pour down the stem of the thermometer, all at once, 15 c.c. of molybdate solution (see p. 402) into the flask. This

will cause the formation of a yellow precipitate containing the phosphorus.

Withdraw the thermometer, cork the flask, and shake it vigorously for about one minute. While shaking the flask, press the fore-finger on the cork to prevent its ejection.

Pour the solution with the yellow precipitate on to a 9 cm. close-texture, smooth-surface filter-paper. Rinse any remaining precipitate into the filter.

Wash the precipitate three times with very dilute nitric acid—1 of nitric acid ($1 \cdot 42$ specific gravity) to 50 of water.

Open out the filter paper, and, with a fine-spout wash-bottle containing warm water, wash the precipitate into a tared porcelain basin or a basin of platinised nickel—see note on p. 378.

Evaporate on the water bath (Fig. 6) till the precipitate is completely dried.

This water bath consists of an oblong copper box with inlet. On the top are two openings cut to suit the size of the evaporating basins. Copper covers are provided for these openings. These have openings to suit the test tubes re quired for dissolving a few samples of steel for carbon estimations. The water supply is stored in a Winchester quart or other glass bottle which is fitted with a two-hole rubber stopper. Glass tubing is arranged as shown in the illustration. To start the bath, the bottle is nearly filled with water, the stopper, with the tubes, is placed in position and set on the wooden stand. On

blowing into the curved glass tube, water is forced through the syphon tube into the water bath, into which it will continue to flow till it rises to the level of the bottom of the curved
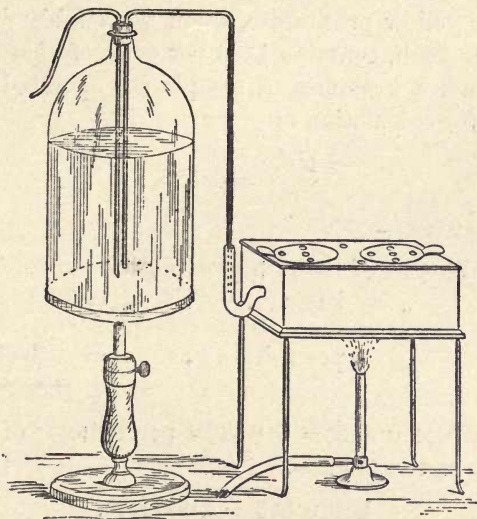
Fig. 6.—Water bath, with constant level water supply.

tube. The water level in the bath will remain practically constant until the supply is exhausted. The bath is mounted on an iron stand, and heat is applied from a Bunsen burner.

Wipe the outside of the basin and allow it to cool. Weigh, and calculate the result.

Other plans are (a) to use counterpoised filter-papers, (b) to brush the dried precipitate

on to a tared watch-glass, and (c) to estimate
by standardised solutions. The author prefers
to wash the precipitate into the tared basin and
dry it on the water bath.

The yellow precipitate, when thoroughly dried on
a water bath, contains 1·63 per cent. of phosphorus,
and when 2 grammes of sample are operated on the
factor for calculation is

$$\frac{1·63}{2} = 0·815.$$

EXAMPLE—   Grammes.
Weight of basin + precipitate = 23·184
   „   basin   .   .   . = 23·125
                                   ———————
   „   precipitate .   . =   0·059
                                   ═══════

0·059 × 0·815 = 0·048 = percentage of phos-
phorus in the sample.

Log 0·815 = $\overline{1}$·9111576.

When phosphorus in steel is estimated in strict
accordance with the foregoing details, the result may
be accepted as reliable.

The following modification has advantages, but
requires practice to ensure concordant results:—
Weigh off 2 grammes of the drillings.
Transfer the weighed portion to a 10·2 × 7 cm.
(4-inch × 2¾-inch) beaker.
Add 40 c.c. of 1·20 specific gravity nitric acid.
Heat till the drillings are dissolved.

Add 10 c.c. of a 1 per cent. solution of potassium permanganate.

Boil till the brown precipitate has dissolved and the pink colour has disappeared.

Cautiously add sulphurous acid (see p. 418) till the solution becomes clear.

Boil off the slight excess of acid and allow to cool.

Add 20 c.c. of 0·88 specific gravity ammonia solution.

Add strong nitric acid till the liquid in the beaker turns to a light sherry colour.

Add not less than 25 c.c. of molybdate solution— prepared by dissolving 100 grammes of ammonium molybdate in 1 litre of water—and, immediately after, add 6 c.c. of strong nitric acid.

The precipitate soon settles, and is filtered, washed, and weighed as in the method described on p. 20.

ESTIMATION BY TITRATION.

Instead of weighing the yellow phospho-molybdate precipitate, it is convenient, when a large number of determinations are to be made, to estimate the phosphorus volumetrically. For this purpose wash the precipitate six times with the usual 2 per cent. nitric acid solution, and afterwards with a 2 per cent. solution of sodium sulphate till free from acid. Open out the filter-paper, and, with a fine-jet wash-bottle containing hot water, wash the precipitate off the paper into a beaker. Measure, from a burette, standard sodium hydrate solution till the precipitate is dissolved, then run in a slight

excess, and note the amount used. Add two or three drops of phenol-phthalein solution to act as an indicator. Then measure, from a burette, standard sulphuric acid or nitric acid solution till change of colour is effected. The solution in the beaker should, of course, be constantly stirred during the addition of the standard acid.

The nitric acid solution may be standardised by pure sodium carbonate (Na_2CO_3), and the caustic soda solution then standardised by the nitric acid. Or, having ascertained the relative strengths of the acid and alkaline solutions, the latter may be standardised by titrating the solution from 2 grammes of steel of known percentage of phosphorus.

Walter Rosenhain states[*] that when the precipitate is washed with water alone the results agree closely with those obtained on washing with nitric acid and ammonium nitrate. His comparative figures show that water-washing gives a slightly higher result.

Rapid Estimation of Phosphorus in Furnace Samples.

For the very rapid approximate estimation of phosphorus in the "metal" in a basic furnace, two previously-prepared solutions are required, viz. :—

No. 1 solution, made by dissolving 200 grammes of ammonium nitrate in about 150 c.c. of hot water, allowing to cool, adding 250 c.c. of strong nitric acid (say 1·4 specific gravity), and making up to 500 c.c.

No. 2 solution, made by dissolving 50 grammes of ammonium nitrate in about 200 c.c. of hot water, allowing to cool, adding 40 grammes of ammonium molybdate dissolved in 200 c.c. of water, and making up to 500 c.c.

A sample of the "metal" is taken from the furnace in a "sample spoon," allowed to solidify, hammered, cooled, drilled, and quickly tested thus :—

Weigh off 0·2 gramme of the drillings.

Transfer the weighed portion to a 15 cm. × 1·6 cm. (about 6 × ⅝ inch) test tube.

Add 4 c.c. of No. 1 solution.

Heat till the drillings are dissolved.

Add 4 c.c. of No. 2 solution.

Warm the solutions.

Shake the tube to facilitate the precipitation.

Compare with the amount of the precipitate from a like quantity of a steel of known percentage of phosphorus which has been similarly treated in a corresponding test tube.

Molybdate and Magnesia Method.

For check analyses, especially in disputed cases, it is advisable to employ a good alternative method, and the one in which the product weighed at the end is pure magnesium pyrophosphate, is, with care and experience, reliable.

Outline of the Process.—A weighed quantity of the sample is dissolved in nitric acid, and evaporated to dryness and roasted. The dried mass, containing the phosphorus in its most highly oxidised

state, is dissolved in acid and neutralised. Nitric acid, ammonium nitrate, and molybdate solutions are added to cause the precipitation of a yellow compound $[(NH_4)_3PO_4.12MoO_3]$ containing all the phosphorus. The yellow precipitate is collected on a filter and washed, thus separating the phosphorus from the other constituents of the steel. The washed precipitate is dissolved in ammonia liquor and the solution is neutralised. Magnesia mixture is then added to precipitate the phosphorus as magnesium-ammonium-phosphate, which is collected, washed, and dried. On ignition it is converted into magnesium pyrophosphate $(Mg_2P_2O_7)$ which is weighed. From the weight of the precipitate the percentage of phosphorus in the steel is calculated.

Details of the Process.—Weigh off 5 grammes of the sample.

Transfer the weighed portion to a 14 × 13 cm. (about $5\frac{1}{2}$ × 5 inch) spouted Jena or Bohemian beaker.

Add 40 c.c. of 1·42 specific gravity nitric acid, along with 10 c.c. of water.

Evaporate on a hot plate to dryness (see note on hot plate, p. 377). When, towards the end of the evaporation, there is much danger of loss by spirting, interpose a thin piece of wire gauze between the plate and the beaker. The evaporation will then proceed more quietly till finished.

Allow the beaker to remain on the hot plate for ten minutes more, so as to oxidise all the phosphorus.

Withdraw the beaker and place it on a cork mat.

When the beaker is not likely to crack in contact

with liquid, add 35 c.c. of 1·16 specific gravity hydro-
chloric acid, and allow to boil until the contents of
the beaker have dissolved.

Continue the boiling till the bulk of the solution
has been reduced to about one-half.

Neutralise the excess acid by cautiously adding
ammonia liquor.

Add more ammonia liquor to form a slight per-
manent precipitate.

Dissolve the precipitate by adding 1·42 specific
gravity nitric acid, and stirring.

Add 35 c.c. of ammonium nitrate solution (see
p. 402).

Heat to 90° C. Immediately raise the thermo-
meter about 2·5 cm. (about 1 inch) clear of the solu-
tion, and pour down the stem of the thermometer, all
at once, about 33 c.c. of molybdate solution (see p.
402) into the beaker. This will cause the formation of
a yellow precipitate containing the phosphorus.

Stir the solution vigorously to hasten precipitation.

Allow to settle at a temperature under 100° C. for
about fifteen minutes.

Pour the solution with the yellow precipitate into
a 9 cm. close-texture filter. Rinse any remaining
precipitate into the filter.

Wash the precipitate three times with very dilute
nitric acid—1 of 1·42 specific gravity nitric acid to 50
of water, collecting the filtrate and washings in a beaker.

Remove the beaker containing the filtrate and
washings, and place a clean 350 c.c. (about 12-oz.)
conical flask under the funnel.

Dissolve the precipitate by means of a dilute

solution of ammonia—say 1 of 0·880 specific gravity ammonia liquor to 8 of water—collecting the solution (and washings) in the conical flask.

Wash four times with dilute ammonia liquor, and twice with warm water.

Heat the solution and washings to about 60° C.

Add 10 c.c. of 0·880 specific gravity ammonia liquor

Add about 5 c.c. of magnesia mixture (see p. 408).

Cork the flask and shake it vigorously for about two minutes. (While shaking the flask, press the cork firmly to prevent its ejection.) This causes the formation of a finely crystalline precipitate of magnesium-ammonium-phosphate, $Mg(NH_4)PO_4.6H_2O$. Allow the precipitate to settle for about an hour.

Decant the clear solution through a 12·5 cm. Swedish filter, and with ammonia water (1 of ammonia 0·880 specific gravity ammonia liquor to 8 of water) wash the precipitate into the filter.

Wash six times with ammonia water as above.

Test the last washings with acidulated silver nitrate (see p. 381).

Wash two or three times with the ammonia water after all the chlorides have apparently been washed out.

Dry the precipitate by placing the funnel, with filter-paper and contents, on a filter dryer (Fig. 4, p. 14), covering with paper, and allowing to dry thoroughly on the hot plate.

Place the dried filter and contents in a tared platinum or porcelain capsule and proceed to ignite. The ignition should be cautiously begun, so as to avoid highly heating the precipitate before the organic part of the filter is burnt away. The residue should be

white (not grey) before removing the capsule to the hottest part of the muffle, where it should remain for an hour. Unless this is done, there is danger of the precipitate so clinging to the filter-paper that it becomes impossible to burn off the paper.

During ignition, the precipitate loses ammonia and water, and is converted into magnesium pyrophosphate ($Mg_2P_2O_7$), thus—

$$2Mg(NH_4)PO_4 . 6H_2O = Mg_2P_2O_7 + 2NH_3 + 7H_2O.$$

Withdraw the capsule and contents and place in a desiccator to cool.

Weigh, and calculate.

The percentage of phosphorus is calculated from the weight of magnesium pyrophosphate, which contains 27·838 per cent. of phosphorus.

When 5 grammes of sample are operated on, the factor for ascertaining the percentage is—

$$\frac{27 \cdot 838}{5} = 5 \cdot 568.$$

Log 5·568 = 0·7456992.

EXAMPLE—

Weight of capsule + ash + precipitate	=	16·3348
„ capsule . . .	=	16·3242
„ ash and precipitate .	=	0·0106
„ filter ash . . .	=	0·0008
„ precipitate ($Mg_2P_2O_7$).	=	0·0098

$$0 \cdot 0098 \times 5 \cdot 568 = 0 \cdot 0546.$$

And **0·055** = percentage of phosphorus in the sample of steel.

ESTIMATION OF PHOSPHORUS IN STEELS
CONTAINING ARSENIC.

From oxidised solutions of steel which contained arsenic and phosphorus the molybdate solution can precipitate compounds of both together.

The late Mr. Walter G. M'Millan pointed out that the presence of 0·01 per cent. of arsenic, if converted into the yellow molybdate precipitate, would calculate out in round numbers as 0·004 per cent. of phosphorus.*

By Prof. Eggertz' method ammonia-phospho-molybdate precipitate free from arsenic may be obtained by precipitating at 40° C., and allowing the precipitate four hours to settle out. The precipitation is not, however, always complete at 40° C. At higher temperatures arsenic is precipitated.

John E. Stead, F.R.S., pre-precipitates the arsenic as sulphide, filters off the solution containing the phosphorus, and in the concentrated filtrate precipitates the phospho-molybdate in boiling solution. His instructive details are, by kind permission, appended.†

METHOD FOR THE DETERMINATION OF PHOSPHORUS.
BY J. E. STEAD.

The method employed for the determination of phosphorus is that known by the name of "The Molybdic Acid Process," in which the phospho-

* *Iron and Steel Institute Journal*, vol. i., 1895, p. 139.
† Report of International Committee submitted to the New York meeting of the Iron and Steel Institute, October, 1904.

molybdate of ammonia after precipitation is weighed and the amount of phosphorus calculated from the weight obtained.

In practice we use two modifications of this method, one in which the steel is dissolved in nitric acid (1·20 sp. gr.), solution decolourised by permanganate of potash, and after the addition of a sufficient quantity of nitrate of ammonia the phosphorus is precipitated with molybdate of ammonia, and the precipitate weighed on a tared filter-paper. This system is very useful for steels containing practically no arsenic and silicon.

In the other method precautions are taken to separate any arsenic which might be present.

4·89 grammes of the steel are dissolved in 35 c.c. of nitric acid of 1·42 specific gravity, and 25 c.c. of hydrochloric acid. The solution is evaporated to dryness, taken up with hydrochloric acid, a little water is added, and afterwards pure granulated zinc in quantities sufficient to completely reduce the ferric chloride to ferrous chloride. When the excess of zinc is dissolved, a few drops of ammonium sulphide are added and the solution is violently agitated. If the black sulphide of iron is not completely dissolved, a little more hydrochloric acid must be added until solution is effected. Sulphide of arsenic precipitates at once and coagulates on shaking, and may be filtered off after vigorous agitation or after standing over-night. After filtering, the residue contains the silica and sulphide of arsenic, the filtrate the phosphorus. The filtrate is oxidised with nitric acid after boiling

off the free sulphuretted hydrogen, and the bulk of liquid is reduced to about 70 c.c. by evaporation. After cooling by placing the beaker in cold water, strong ammonia is added until the solution is just neutral, then 8 c.c. of the same ammonia in excess. Nitric acid is now added until the hydrated oxide of iron has just passed into solution, and a final addition of 5 c.c. nitric acid is added. If the volume of liquid is greater than 100 c.c. it may be evaporated until reduced to that bulk. When boiling, 20 c.c. of a 10 per cent. solution of molybdate of ammonia in water* are added, and the beaker with contents well shaken and allowed to stand on the table to allow the phospho-molybdate of ammonia to completely separate. When the supernatant liquid is perfectly bright, and the precipitate has settled to the bottom, the solution is filtered through tared filter-papers. These latter are made in the following manner, viz. :—Two folded papers, after thoroughly drying in a water oven, are placed on opposite pans of an accurately adjusted balance. From the heavier paper portions are clipped off the apex until one filter counterpoises the other. They are then returned to the water oven for fifteen to twenty minutes. They are then taken out, and final and accurate adjustment made. The whole filter is placed inside the other, and in this the precipitate is collected.

After washing the precipitate with water containing 1 per cent. nitric acid, it is given three

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* Please note that this solution differs from the one directed to be used for other phosphorus estimations.

washings with distilled water. The filter with contents is then dried at about 110° C.

After drying thoroughly, the filters are separated, the counterpoise paper being placed on one pan, and the paper with precipitate on the other. Weights are added to the pan with the counterpoise paper until equilibrium is established. The weight thus obtained divided by three gives the exact percentage of phosphorus present in the original metal.

ESTIMATION OF MANGANESE IN STEEL.

GRAVIMETRIC METHOD.

Outline of the Process.—The weighed sample of the steel is dissolved, and the excess acid is carefully neutralised. A large quantity of water and a measured amount of ammonium acetate solution are added. On boiling, a bulky precipitate consisting of basic hydrate and acetate of iron is formed, and the solution containing the manganese is separated on filtering and washing. The manganese in the filtrate is peroxidised by the action of bromine.

On addition of ammonia, manganese hydrate is precipitated. This is collected, washed, and ignited. The percentage of manganese is ascertained from the weight of the finished residue of Mn_3O_4.

This method of estimating manganese has been objected to on the ground that the ignited precipitate may vary in composition. With care this need not be so, and the process, as here detailed, is regularly employed in leading iron and steel works for the estimation of manganese in steels, spiegel-eisen, and ferro-manganese. A process which yields concordant results over such a wide range—results acceptable alike to buyers and sellers—cannot consistently be classed as unreliable.

Details of the Process.—Weigh off 2 grammes of the sample. Transfer the weighed portion to a 1,200 c.c. (about 40-oz.) globular Bohemian flask.

Add 15 c.c. of 1·42 specific gravity nitric acid along with 7 c.c. of water. Prof. Arnold recommends hydrochloric acid for dissolving tool steel.

Set the flask on a hot plate to hasten solution.

When the sample has dissolved add about 20 c.c. of hot water, and boil.

Add ammonia solution till a slight permanent precipitate forms and remains in the hot liquid even after violent shaking. Much of the success of the estimation depends on the accuracy with which the neutralisation is effected.

Add about 600 c.c. of cold water.

Add 35 c.c. of ammonium acetate solution (see p. 401).

From this point the process is also applicable to the gravimetric estimation of manganese in pig iron.

Boil briskly over the flame of a 16 mm. (about ⅝-inch) Bunsen burner. If the Bohemian flask is set on a tripod, the top of which is of stout iron wire, the contents may be boiled over a large Bunsen flame, no gauze being required. When the top of the tripod has sharp edges such procedure is risky.

Prepare a 28 cm. (about 11-inch) folded filter of No. 598 C. S. and S. or other thick filter-paper, place it in an 18 cm. (about 7-inch) funnel, saturate it with hot water, and place it in a large

filter stand—see Fig. 7. Set under it a 1,200 c.c. (about 40-oz.) Phillips' conical beaker on a dry cork mat.

Allow the *boiling* to continue for about half a minute. If the liquid nearly froths over, remove the flask till the brisk action ceases, replace on the tripod, and allow the rapid boiling to continue. It
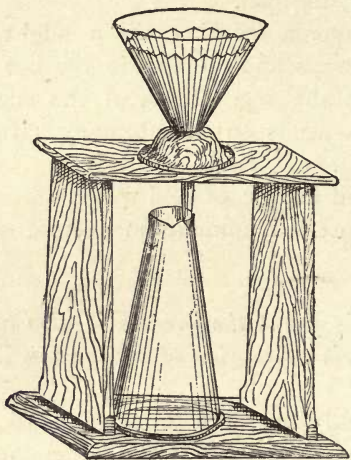
Fig. 7.—Stand, &c., for large funnel.

may be necessary to remove and replace two or three times. A voluminous brown or chocolate-coloured precipitate should be formed, from which a clear colourless liquid should drain away quickly when on the filter.

Immediately the boiling has finished, pour the contents of the flask on to the prepared filter, taking

care not to rest the neck of the hot flask on the edge of the glass funnel, or the former may crack.

Rinse the flask twice with hot water and pour the rinsings on to the filter. Allow the liquid to drain off thoroughly into the beaker flask.

Wash three times with hot water, collecting the washings in the beaker flask. If the operations have proceeded smoothly, filtering and washing may easily be completed within an hour.

Cool the filtrate and washings.

Add about 4 c.c. of bromine to peroxidise the manganese. Stir well while adding the bromine, and until it is all dissolved. The rubber tip of the stirring rod must be kept from contact with the drops of bromine, and should not be kept in the brominated liquid.

Allow to stand for about 15 minutes after brominating.

Cautiously add about 30 c.c. of strong ammonia solution.

Stir well, and allow to stand for a few minutes.

Boil till most of the excess ammonia has been driven off. Boiling hastens the precipitation of hydrated manganese peroxide, and filtering is facilitated by driving off the excess ammonia.

Filter through a 12·5 cm. Swedish filter-paper, and wash four times with hot water.

Place the funnel containing the filter-paper and precipitate on a dryer on a hot plate (see Fig. 4, p. 14), and allow to remain till dried.

Ignite the dried paper and precipitate in a tared platinum or porcelain crucible in a muffle furnace
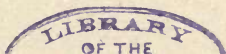
which is at a white heat. Allow to remain in the hot muffle for 30 minutes at least.

Allow to cool in a desiccator, weigh, and note the weight.

Correction for Co-precipitated Iron.

A small quantity of ferric oxide usually accompanies the manganese oxide, and may be easily estimated by colour, in the following manner:—

Transfer the weighed substance to a 60 c.c. (about 2-oz.) Bohemian beaker.

Add about 10 c.c. of hydrochloric acid, and boil till the precipitate has dissolved.

Add about 5 c.c. of a 10 per cent. ammonium sulpho-cyanide solution.

If the mixture shows only a faint colouration, no correction is necessary.

If the mixture shows a decided colour, add about 10 c.c. of cold water, and pour the solution into a 100 c.c. stoppered graduated cylindrical measure. Rinse the beaker, and pour the rinsings into the measure. Mix well.

Measure 20 c.c. of standard iron solution (= 0·0005 gramme of ferric oxide, see p. 408) into a corresponding stoppered graduated glass having a distinguishing mark. Add 5 c.c. of the 10 per cent. sulpho-cyanide solution, and mix well.

Compare the depth of colour of the solutions.

Dilute the more highly-coloured solution, so as to bring each to the same depth of colour.

Calculate the weight of the co-precipitated ferric oxide, thus—

Divide the weight of ferric oxide in the standard solution by its volume, and multiply the product by the volume of the solution of the oxides from the manganese estimation.

EXAMPLE.—Fe_2O_3 in standard solution = 0·0005 gramme diluted to 25 c.c.

Solution of oxides diluted to 40 c.c.

$$\frac{0·0005}{25} = \times 40 = 0·0008.$$

0·0008 = weight of co-precipitated ferric oxide.

Calculate the percentage of manganese.

On igniting the precipitate as directed, the manganese peroxide is converted into Mn_3O_4. Mn_3O_4 contains 72·052 per cent. of manganese, and when 2 grammes of sample have been operated on the factor for calculation is

$$\frac{72·052}{2} = 36·026.$$

EXAMPLE—

		Gramme.
Weight of Mn_3O_4 + Fe_2O_3 + filter ash	=	·0164
„ filter ash	=	·0008
„ Mn_3O_4 + Fe_2O_3 . . .	=	·0156
„ Fe_2O_3	=	·0008
„ Mn_3O_4	=	·0148

0·0148 × 36·026 = 0·53 = percentage of manganese in the sample of steel.

Log 36·026 = 1·5566160.

Estimation of Manganese in Steel.

Colorimetric Method

suggested by Mr. Hugh Marshall. Details of process by Mr. Harry E. Walters, Duquesne Steel Works.*

Outline of the Process.—When steel containing manganese is dissolved in nitric acid, and silver nitrate and ammonium persulphate afterwards added, a pink colour is developed, the depth of which depends on the amount of manganese present. This is compared with the colour from an equal weight of steel containing a known percentage of manganese.

Details of the Process.—Weigh off a suitable quantity of the sample. If the steel is supposed to contain 0·75 per cent., or over, 0·1 gramme should be taken; if the supposed percentage is less, 0·2 gramme should be weighed off.

Transfer the weighed portion to an 18 × 1·6 cm. (about 7 × ⅝ inch) test tube.

Weigh off an equal quantity of a suitable standard steel and transfer to a similar test tube.

Add to each 10 c.c. of nitric acid of 1·2 specific gravity. If 0·1 gramme of steel has been taken, 6 c.c. of nitric acid will suffice.

Place the test tubes in a water bath (see Fig. 6, p. 21), and heat until the steels have dissolved and all nitrous fumes are driven off.

Add 15 c.c. (or 10 c.c. for 0·1 gramme of steel) of a 0·133 per cent. solution of silver nitrate (= 0·02

* Proceedings of Engineers' Society of Western Pennsylvania.

gramme of $AgNO_3$ in 15 c.c.). This will cool the solution to the temperature at which the next reagent should be added.

Immediately add to each about 1 gramme of previously moistened persulphate (see note on persulphate, p. 419).

Continue heating in the water bath till oxidation commences, then for about half a minute longer.

Remove the tubes from the bath while the evolution of gas continues, and place them in a cold-water bath.

When the solutions have cooled, transfer the coloured solution from the standard steel to a marked Eggertz' tube, make up with cold water to a suitable volume, and mix thoroughly.

Transfer the coloured solution from the other steel to a corresponding Eggertz' tube, and compare with the standard solution.

NOTE.—In comparing the tints, the graduated tubes are placed side by side, so that diffused light coming through ground glass or a sheet of moistened filter-paper will pass through the solutions. Change the relative positions of the tubes—standard tube to the right, and sample tube to the left, and *vice versâ*—during the comparison.

Dilute the darker coloured solution with cold distilled water as far as necessary, mix well, and compare again.

When the solutions in each tube agree in depth of colour, note the volumes, and calculate the percentage of manganese.

GENERAL RULE FOR CALCULATING.—Divide the percentage of manganese in the standard steel by the volume of its solution, and multiply the product by the volume of the solution of the steel which is being tested.

EXAMPLE.—Standard steel contained 0·52 per cent. of manganese, and the solution was diluted to 20·8 c.c. The solution from the sample of steel being tested required to be diluted to 23·2 c.c.

Then $\dfrac{0\cdot 52}{20\cdot 8} \times 23\cdot 2 = 0\cdot 58,$

and 0·58 = percentage of manganese in the sample of steel.

ESTIMATION OF SULPHUR IN STEEL.

Evolution and Gravimetric Method.

Outline of the Process.—The weighed sample is placed in a properly-fitted evolution flask, and acid is added so as to cause the sulphur to be converted into sulphuretted hydrogen, which, as it bubbles through a solution of copper sulphate, forms a precipitate of copper sulphide. The sulphide is separated on a filter, washed thoroughly, dried, ignited, and the residue weighed.

The reactions may be conveniently summarised in the following equations, when $R = Mn$ or Fe :—

$$RS + 2HCl = RCl_2 + H_2S.$$
$$H_2S + CuSO_4 = CuS + H_2SO_4.$$
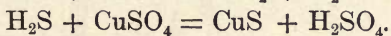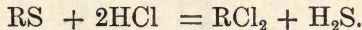
The washed and dried copper sulphide, on being strongly heated with access of air, is oxidised.

$$2CuS + 3O_2 = 2CuO + 2SO_2.$$
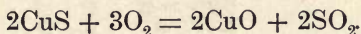
From the weight of the copper oxide the quantity of sulphur which was present is deduced.

Details of the Process.—Weigh off 5 grammes of the sample.

Transfer the weighed portion to a 300 c.c. (about 10-oz.) conical flask which has been fitted with a rubber cork carrying a safety funnel, condenser, and delivery tube arranged as shown in Fig. 8 (see next page).

Moisten the cork, and insert it in the neck of the flask.

Direct a jet of water between the cork and the curvature of the flask rim.

With a spiral motion press the cork firmly into the neck of the flask, so as to make a good gas-tight joint.

Pour about 50 c.c. of cold saturated solution of copper sulphate into a 7-inch × 1-inch (18 × 2·5 cm.) test tube or beaker.
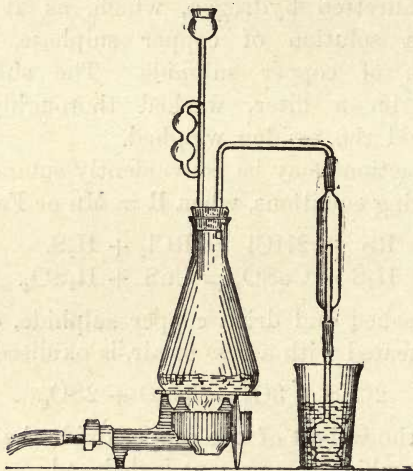
Fig. 8.—Flask, &c., for sulphur evolution.

Arrange the apparatus so that the condensing delivery tube dips into the solution.

Pour about 40 c.c. of 1·16 specific gravity pure hydrochloric acid into the safety funnel.

If necessary, lessen the back pressure by momentarily raising the flask, &c., but not the test tube. This will facilitate the flow of acid into the flask.

A large quantity of gas, from the decomposition of carbide, is evolved along with the sulphuretted hydrogen. Slow evolution leads to a low result. The gases should be caused to come off at a fairly rapid rate.

When brisk action has subsided, pour 40 c.c. of hot water through the safety funnel into the flask.

When the action has somewhat slackened, light the burner—still permitting the gases to come off through the copper sulphate solution—and allow to remain there until all the steel has dissolved, and the solution in the flask has boiled for one or two minutes.

Detach the delivery tube.

Filter off the copper sulphide, using a 12·5 cm. Swedish (but not an "ashless") filter.

Wash any adhering sulphide from the delivery tube on to the filter.

Wash the copper sulphide about twelve times with hot water. This precipitate should be washed quickly. It is difficult to wash all the copper sulphate through an ordinary filter; it is more difficult to wash it from an "ashless" filter.

Dry the precipitate and filter.

Ignite in a tared porcelain capsule, at first gently in a muffle, and then for 30 minutes in a moderately hot part of the muffle.

Allow the crucible and contents to cool in a desiccator.

Weigh, and calculate the percentage of sulphur in the steel.

EXAMPLE.—Weight of sample taken = 5 grammes.

Weight of capsule + ash + precipitate = 8·3143
,,   capsule   .   .   .   . = 8·3070

,,   ash + precipitate   .   . = 0·0073
,,   ash .   .   .   .   . = 0·0008

,,   precipitate   .   .   . = 0·0065

Atomic weight of sulphur   = 32·06.
Molecular weight of $CuO = 63·6 + 16 = 79·6$.

$$\frac{32·06}{79·6} = 0·402764.$$

0·402764 = weight of S deduced from weight of CuO.

The factor for 5 grammes is

$$\frac{100}{5} \times 0·402764 = 8·0553.$$

Weight of ignited precipitate = 0·0065.

0·0065 × 8·055 = 0·052 = percentage of sulphur in the sample of steel.

It is not unusual to make a duplicate estimation on either 4 or 6 grammes.

Factor for 4 grammes = 10·07.
,,   6   ,,   = 6·71.

ESTIMATION OF SULPHUR IN STEEL.

VOLUMETRIC (IODINE) METHOD.

Outline of the Process.—The sulphur is evolved as sulphuretted hydrogen, which is caught in a solution of caustic soda or caustic potash. This is afterwards more than neutralised with sulphuric acid, and titrated with standard iodine solution, starch being used as an indicator.

The changes which take place are :—

(1) The sulphur present, as sulphide, combines with hydrogen of the acid used for dissolving the steel, and sulphuretted hydrogen is evolved.

(2) The sulphuretted hydrogen is caught in caustic alkali solution, and held there as alkaline sulphide.

(3) On the caustic liquid being acidified, sulphuretted hydrogen is again formed, and is retained in the solution.

When $R = Mn$ or Fe the reactions may be thus expressed :—

$$(1) \ RS \ \ + 2HCl \ \ = RCl_2 \ \ + H_2S.$$
$$(2) \ H_2S \ + 2NaHO = 2H_2O \ \ + Na_2S.$$
$$(3) \ Na_2S + H_2SO_4 \ = Na_2SO_4 + H_2S.$$
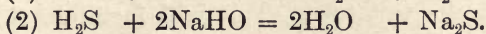
The quantity of sulphur present is then estimated as a result of the reaction :—

$$H_2S + I_2 = 2HI + S.$$

Addition of iodine in excess of that required for the completion of the reaction gives a permanent blue colour with starch solution.

STANDARDISING THE IODINE SOLUTION.—Having prepared the solutions, the iodine solution is standardised thus :—

Weigh off 5 grammes of steel drillings containing a known percentage of sulphur.

Transfer the weighed portion to a 300 c.c. (about 10-oz.) conical flask, which is fitted with a rubber cork carrying a safety funnel and a delivery tube.

Moisten the cork. and insert it in the neck of the flask.

Direct a jet of water between the cork and the curvature of the flask rim.

With a spiral motion press the cork firmly into the neck of the flask, so as to make a good gas-tight joint.

Pour about 50 c.c. of the prepared caustic soda solution (see p. 415) into a beaker or an 18 cm. × 2·5 cm. (about 7-inch × 1-inch) test tube.

Arrange the apparatus so that the condensing delivery tube dips into the solution, as shown in Fig. 8, p. 44.

Pour about 40 c.c. of pure 1·16 specific gravity hydrochloric acid into the safety funnel. Lessen the back pressure by momentarily raising the flask, &c., but not the test tube. This will facilitate the flow of the acid into the flask. A large quantity of gas, from the decomposition of carbide, is evolved along with the sulphuretted hydrogen. Slow evolution leads to a low result. The gases should be caused to come off at a fairly rapid rate.

When brisk action has subsided, pour 40 c.c. of hot water through the safety funnel into the flask.

When the action has somewhat slackened, light the

burner—still allowing the gases to come off through the caustic soda or potash solution—and allow to remain there until all the steel has dissolved and the solution in the flask has boiled for one or two minutes.

Detach the delivery tube, and rinse it into a 7-inch porcelain basin.

Empty the solution from the beaker or test tube into the same basin.

Wash the beaker or test tube, collecting the washings also in the basin.

Add 30 c.c. of dilute sulphuric acid (see p. 417) and about 5 c.c. of the freshly-prepared but cold starch solution (see p. 416).

From a burette filled to zero, carefully run standard iodine solution (see p. 407) into the basin while stirring briskly. When a decided violet colour appears which is somewhat persistent, add the iodine solution carefully drop by drop, and, when a distinct violet colour remains for about a minute after the addition of one of the drops, read off and note the volume of iodine solution used.

Correction for Quantity of Iodine Solution required to show Colour in the Solutions used.

Into a 7-inch porcelain basin put

About 50 c.c. of the caustic soda solution.

   „   30 c.c. of the dilute sulphuric acid solution.

   „   50 c.c. of cold, distilled water, and

   „   5 c.c. of the starch solution.

Run in, cautiously, standard iodine solution (stirring meanwhile), until a violet colour of the

same depth as in the other basin appears and remains.

Read off the quantity taken, and deduct from the quantity used in the former titration.

Duplicate the sulphur estimation, using 4 grammes of the steel.

If the results are fairly concordant, they may be accepted; if the difference is too great, make another estimation, using $4\frac{1}{2}$ grammes of the steel.

CALCULATION FOR STANDARDISING.

5 grammes of the steel (which was known to contain ·046 per cent. of sulphur) required 9·4 c.c. of the standard iodine solution, and the blank experiment required 0·3 c.c.

∴ The H_2S from the steel required = 9·1 c.c.

$$\frac{0·046 \times 5}{100} = 0·0023.$$

$$\frac{0·0023}{9·1} = 0·0002527 = \text{result of 1st estimation.}$$

7·43 c.c. (after correction for blank) of the standard iodine solution were required for 4 grammes of the steel.

$$\frac{0·046 \times 4}{100} = 0·00184.$$

$$\frac{0·00184}{7·43} = 0·0002476 = \text{result of 2nd estimation.}$$

Result of 1st estimation = 0·0002527.
Result of 2nd estimation = 0·0002476.

Average of the two estimations = 0·0002502.

The bottle containing the solution is therefore labelled "Standard iodine solution: every c.c. = ·0002502 gramme of sulphur. Deduct for blank 0·3 c.c."

If the solution is kept in stock for a time, it should be restandardised before using again. If in regular use, restandardise every third day.

ESTIMATION OF SULPHUR IN A SAMPLE OF STEEL BY THE VOLUMETRIC (IODINE) METHOD.

Weigh off 5 grammes of fine drillings taken through such a depth of the sample as required for a fair average.

Proceed exactly as in standardising.

Note the volume of the standard iodine solution required, and deduct the volume required for the blank.

Duplicate on 4 grammes.

Calculate the results.

EXAMPLE OF CALCULATION.—5 grammes of the steel sample required 10·1 c.c. of the standard iodine solution.

The blank was ·33, therefore the standard iodine solution required for the sample steel was 9·77 c.c.

Every c.c. of the iodine solution = ·0002502 gramme of sulphur.

$$\frac{·0002502 \times 100 \times 9·77}{5} = ·005004 \times 9·77 =$$

0·049 = percentage of sulphur in sample of steel.

Cadmium and Iodine Method.

Instead of using a solution of caustic soda, the evolved sulphuretted hydrogen may be caught in a solution of cadmium chloride prepared as directed on p. 404. Cadmium sulphide is precipitated, and is afterwards dissolved and estimated by titrating with standard iodine solution. The apparatus is fitted up as shown in Fig. 8 (p. 44), except that a larger beaker is employed to hold the 20 c.c. of 2 per cent. cadmium chloride solution and 200 c.c. of cold water. 5 grammes of the sample are treated with acid and water, and the gases evolved are led into the cadmium chloride solution. When evolution is complete, 10 c.c. of cold starch solution and 25 c.c. of 1·16 specific gravity hydrochloric acid are added to the contents of the beaker. For starch solution see p. 416.

When the whole is cold, standard iodine solution (see p. 407) is measured in till a permanent blue colour is obtained.

An advantage of this method is that one may, with practice, approximately gauge the percentage of sulphur in the sample before titrating.

The procedure, precautions, method of standardising, and calculating are all as described in the preceding pages.

At the National Physical Laboratory, Bushy Park, London, the volumetric estimation of sulphur is carried out thus: *—The steel drillings are dissolved in the evolution flask of this apparatus in hydrochloric acid of 1·10 specific gravity, the operation being aided

* Rosenhain, *Iron and Steel Institute Journal*, vol i., 1908.

by heat, although boiling the acid is avoided. The evolution flask and entire apparatus are filled, prior to the commencement of the operation, with an atmosphere of carbon dioxide, obtained by passing a stream of this gas, derived from a cylinder of liquid carbonic acid, through the entire apparatus. The evolved gases, aided towards the end of the operation by a further stream of carbonic acid, are bubbled through an absorption flask containing a solution of cadmium acetate strongly acidified with acetic acid (25 grammes pure cadmium acetate and 10 per cent. glacial acetic acid per litre); after passing this flask the gases pass through a narrow-bore tube of vitreous silica heated to redness by a Bunsen burner with a flat flame, the gases passing finally through a second cadmium acetate absorption flask and then away to the fume-chamber. When the steel has completely dissolved, the contents of the two absorption flasks are mixed and the yellow sulphide of cadmium is filtered off; this is a rapid operation since the flask need not be washed carefully—the operation is merely intended to separate the sulphide from the bulk of the absorption liquid. As soon as this has been done the precipitate is washed from the filter back into the original flask, and there dissolved in 10 c.c. of standard iodine solution, the action being aided by the introduction of a small quantity of hydrochloric acid. The excess of iodine is then titrated by means of sodium thiosulphate and starch. It is to be observed that while this titration can be carried out in the liquid of the absorption flasks without filtration, it has been found that this leads to occasional discrepancies in the

results. Apparently, particularly in the case of high-carbon steel, the evolved gases carry into the absorption flask something which is capable of absorbing iodine, but which is not sulphur; this disturbing substance can be eliminated by the filtration described above.

The following table, which contains typical examples from a wide range of steel, shows the closeness of the agreement observed between the results of this evolution method and the oxidation method:—

Steel.			Lab. No.	Percentage of Sulphur found by	
				Evolution.	Gravimetric.
Tyre,	.	.	896	0·042	0·044
Tyre,	.	.	936	0·046	0·049
Tyre,	.	.	952	0·045	0·049
Shaft,	.	.	...	0·041	0·043
Tyre,	.	.	969	0·014	0·013
Plate,	.	.	980	0·048	0 045
Joist,	.	.	1018	0·054	0·052
Joist,	.	.	1054	0·062	0·063

ESTIMATION OF SULPHUR BY OXIDATION AND PRECIPITATION AS BARIUM SULPHATE.

Outline of the Process.—The weighed sample is dissolved in acid and oxidised. It is again dissolved, and, on addition of barium chloride solution, barium sulphate is precipitated. This is collected on a filter, washed, dried, and weighed. From the ascertained weight the percentage of sulphur is calculated.

Details of the Process.—Weigh off 3 grammes of the sample.

Transfer to a 3-inch × 1-inch platinum basin.

Add sufficient concentrated nitric acid, in small instalments, to dissolve the sample. Keep the basin covered with a watch-glass during the period of dissolving.

When completely dissolved, add 2 grammes of potassium nitrate.

Evaporate to dryness.

Ignite at a red heat.

When cool, add 50 c.c. of a 1 per cent. solution of sodium carbonate.

Gently boil for a few minutes.

Filter, collecting the filtrate (and washings) in a 7·5 × 5 cm. (about 3-inch × 2-inch) beaker.

Wash with hot 1 per cent. sodium carbonate solution.

Add hydrochloric acid to acidify the filtrate.

Evaporate to dryness.

When the beaker has cooled, add 5 c.c. of hydrochloric acid in 45 c.c. of water.

Boil briskly for five minutes.

Filter, collecting the filtrate (and washings) in a 10 × 7·5 cm. (about 4-inch × 3-inch) beaker.

Wash thoroughly with hot water containing about 2 per cent. of hydrochloric acid.

Add 5 c.c. of a 10 per cent. solution of barium chloride. This should precipitate all the sulphur as barium sulphate according to the equation—

$$K_2SO_4 + BaCl_2 = BaSO_4 + 2KCl.$$

Filter through a close-texture filter-paper.

Wash well with hot water.

Test some of the last washings by collecting in a clean test tube, and adding a few drops of clear acidified silver nitrate solution.

Wash twice after all the chloride appears to have been washed out.

Dry the precipitate on the filter.

Ignite in a tared crucible for half an hour in a hot muffle.

Weigh and calculate.

EXAMPLE—

Grammes.

Weight of crucible + ash + precipitate .	=	16·8504
„ crucible	=	16·8308
„ ash + precipitate . . .	=	0·0196
„ ash	=	0·0010
„ precipitate ($BaSO_4$) . .	=	0·0186

Percentage of S in $BaSO_4$ = 13·73.

$$\frac{13\cdot73}{5} = 2\cdot746 = \text{factor when 5 grammes of sample}$$

are taken.

$$0\cdot0186 \times 2\cdot746 = 0\cdot051.$$

0·051 = percentage of sulphur in the sample of steel.

ANALYSIS OF PIG IRON.

ESTIMATION OF COMBINED CARBON.

EGGERTZ' COLORIMETRIC METHOD.

Outline of the Process.—This method is based on the fact that when iron which contains carbon in a certain state of combination is dissolved in dilute nitric acid, a yellow-coloured solution is obtained, and the depth of the colour is, within limits, in proportion to the amount of carbon present in that state of combination.

In practice a weighed quantity of a standard steel is dissolved, the solution diluted to a definite volume in a graduated Eggertz' tube, and mixed well. A like quantity of the sample of pig iron to be tested is dissolved and filtered, and the filtered solution is carefully diluted in a corresponding graduated tube till the solution shows the same depth of colour. A short calculation then gives the percentage.

Details of the Process.—Weigh off 0·1 gramme of a suitable standard.

> As a standard, steel is preferable to pig iron, even against the well-founded belief that steel should be tested against steels of their own class.

Suitable standards :—

> For Grey iron,   0·50 per cent. carbon steel.
> „ Mottled iron, 1·00   „   „
> ,   White iron, 1·40   „   „

Transfer the weighed portion to a clean, dry 13 × 1·3 cm. (5 inches × ½ inch) test tube with a distinctive label or mark on it. A rubber ring makes a suitable distinction for the standard tube.

Weigh off 0·1 gramme of the sample of pig iron to be tested.

Transfer the weighed portion to a similar test tube with a distinctive label or mark on it.

To each weighed quantity add nitric acid solution of 1·2 specific gravity.

> If 0·5 standard, .   .   .   2   c.c.
> „ 1·0   „   .   .   .   2·5 c.c.
> „ 1·4   „   .   .   .   3·0 c.c.

When brisk action has ceased, set the test tubes, with contents, in a bath of boiling water, and keep at boiling point for twenty minutes. The rack and stand shown in Figs. 1 and 2 (pp. 3 and 5) are convenient.

Withdraw the test tubes from the hot bath.

Immediately filter the solution from the pig iron through a 7 cm. filter into a 20 c.c. Eggertz' tube. Rinse the test tube with warm water, collecting the washings, through the filter, in the same Eggertz' tube.

If the solution is not promptly filtered, as directed, a coloured precipitate may settle out and spoil the estimation.

Label the Eggertz' tube.

Allow to cool.

Drain the cold standard solution from the test tube into a corresponding Eggertz' tube, which has a distinguishing mark, such as a rubber ring or a mark made with a diamond. Rinse into the Eggertz' tube with a fine jet of cold water.

Make up to a definite measure with cold water.

Close the graduated tube, and shake it so as to thoroughly mix the fluids.

Compare the depth of colour of the two solutions.

NOTE.—In comparing the tints, the graduated tubes are placed side by side, so that diffused light coming through ground glass or a sheet of moistened filter-paper will pass through the solutions. Change the relative positions of the tubes—standard tube to the right, and sample tube to the left, and *vice versâ*—during the comparison.

Dilute the darker-coloured solution with cold water, mix well, and compare again.

If necessary, dilute further, mix, and compare.

Repeat until the solution from the sample is of the same depth of tint as that of the standard.

When the solutions in the Eggertz' tubes are of the same depth of colour, read off the volumes of the solutions, and calculate the result.

EXAMPLE.—Standard material contained 0·63 per cent. of combined carbon; solution was diluted to 6·3 c.c.

Sample required to be diluted to 7·8 c.c.

∴ Combined carbon in the sample of pig iron = 0·78 per cent.

For other examples of calculations, see pp. 7 and 8.

ESTIMATION OF GRAPHITIC CARBON IN PIG IRON.

Outline of the Process. — To the weighed sample in a beaker acid is added and evaporated to dryness. During the evaporation the silicon is oxidised to silica. Acid is again added, and, after boiling for a few minutes, the insoluble residue from an ordinary pig iron consists of silica and graphite only. These are separated from the soluble constituents by filtering and washing. The washed residue is transferred to a tared basin, dried on a steam bath, and the weight ascertained. On ignition, the graphite is burned off, and, after cooling, the fixed residue is weighed. The weight of the graphite is found by difference, and the percentage is calculated.

Details of the Process.—Weigh off 2 grammes of the sample.

Transfer the weighed portion to a 12·5 × 9·7 cm. (about 4¾ × 3¾ inches) Bohemian or Jena beaker.

Add 30 c.c. of 1·16 specific gravity hydrochloric acid.

Evaporate on a hot plate till the residue in the beaker is quite dry (see note on "hot plate," p. 377).

Withdraw the beaker and place it on a cork mat.

When the beaker is not likely to crack in contact with liquid, add 40 c.c. of hot water and 15 c.c. of 1·16 specific gravity hydrochloric acid.

Boil until the iron has dissolved.

Filter through a 12·5 cm. Swedish filter.

Wash three times with acidulated water—1 of 1·16 specific gravity hydrochloric acid to 6 of water.

Wash three or more times with hot water.

Allow to drain thoroughly.

With a fine-jet wash bottle wash the insoluble matter from the filter into a tared platinum or porcelain basin of 7·6 cm. (or about 3 inches) diameter.

Evaporate on a water bath, and complete the drying in a steam oven.

Allow to cool in a desiccator.

Weigh and note the weight.

Ignite the residue. Let the basin remain in the muffle until a pure white, or faintly pink or reddish, residue is left. The residue (silica) should be white, but even a slight trace of iron will impart a colour.

Withdraw the basin and contents, and allow to cool until the basin can be lifted by hand.

Complete the cooling in a desiccator.

Weigh again and calculate.

EXAMPLES.—

(a) When the percentage of silicon is not required.

Weight of capsule + residue,   Grammes.
   before ignition,   .   .   .   = 27·4374
Weight of capsule + residue, after
   ignition, ...   = 27·3850

Loss on ignition = weight of graphite   0·0524

2 grammes of sample were taken for estimation.

$$\frac{100}{2} \times \cdot 0524 = 2\cdot 62.$$

2·62 = percentage of graphite in the sample of pig iron.

(b) When the percentage of silicon is required.

EXAMPLE—

Weight of basin + insoluble   Grammes.
   matter, after drying,   .   .   = 27·4374
Weight of basin .   .   .   .   = 27·3185
Weight of insoluble matter, after
   drying (*graphite and silica*),   .   =   0·1189

Weight of basin + insoluble   Grammes.
   matter, after ignition,   .   .   = 27·3850
Weight of basin .   .   .   .   = 27·3185
Weight of insoluble matter, after
   ignition (*silica*),   .   .   .   =   0·0665

	Grammes.
Weight of insoluble matter, before ignition, ... =	0·1189
Weight of insoluble matter, after ignition, ... =	0·0665
Loss on ignition (*graphite*) . . =	0·0524

To find percentage of graphite (2 grammes taken)—

$$\frac{100}{2} \times \cdot 0524 = 2 \cdot 62.$$

2·62 = percentage of graphite.

To find percentage of silicon :—

The ignited pure residue (SiO_2) contains 47·02 per cent. of silicon, and when 2 grammes of sample are operated on, the factor for calculation is

$$\frac{47 \cdot 02}{2} = 23 \cdot 51.$$

EXAMPLE—

		Grammes.
Weight of silica + crucible =	18·2783
„ crucible . . =	18·2118
„ silica . . =	0·0665

0·0665 × 23·51 = 1·56 = percentage of silicon in the sample.

Log 23·51 = 1·3712526.

Estimation of Total Carbon in Pig Iron.

(*a*) Add together the percentage of combined carbon and of graphitic carbon; or

(*b*) Estimate by combustion, as described on pp. 98 to 115.

ESTIMATION OF SILICON IN PIG IRON.

If it is intended to estimate silicon, phosphorus, and manganese in the sample of pig iron, the method described on pp. 74 to 77 should be adopted, but when silicon alone is to be determined the following method is recommended.

Outline of the Process.—When pig iron is dissolved in acid and the solution is evaporated to thorough dryness, the silicon (Si) becomes oxidised to silica (SiO_2). After boiling for a few minutes in hydrochloric acid, the insoluble residue from an ordinary pig iron consists of silica and graphite only. These are separated from the soluble constituents by filtering and washing. The insoluble residue is collected on a filter, washed, dried, ignited till all the graphite has been burned off, and weighed. The percentage is then calculated.

Details of the Process.—Weigh off 2 grammes of the sample.

Transfer the weighed portion to a 12·2 × 9·7 cm. (about $4\frac{3}{4}$ × $3\frac{3}{4}$ inches) Bohemian or Jena beaker.

Add 15 c.c. of hydrochloric acid of 1·16 specific gravity along with 15 c.c. of nitric acid.

Evaporate on a hot plate (see p. 377) till the residue in the beaker is quite dry, then allow to stand on the hot plate for about ten minutes more to complete the oxidation of the phosphorus.

Withdraw the beaker and place it on a cork mat.

When the beaker is not likely to crack in contact with liquid, add about 20 c.c. of 1·16 specific gravity hydrochloric acid and evaporate to about half bulk.

Add about 20 c.c. of hot water, and boil for two minutes.

Filter the solution through a 12·5 cm. Swedish filter-paper.

Wash the residue (silica and graphite) well, first with dilute hydrochloric acid—say 1 of 1·16 specific gravity acid to 6 of water—and afterwards with hot water as often as required.

All traces of colour should be removed from the filter-paper and the precipitate. If washing does not effect this, the residue must be afterwards purified by fusion (see p. 16) or treated with hydrofluoric acid, which causes the volatilisation of silica (see next page).

Dry the residue by placing the funnel with filter-paper and contents on a filter dryer (Fig. 4, p. 14), covering with paper, and allowing to dry on the hot plate.

Place the dried residue and filter-paper in a tared platinum or porcelain crucible or capsule.

Ignite in a hot muffle.

Withdraw the crucible, or capsule, and contents, and allow to cool in a desiccator.

Weigh quickly and note the weight.

Examine the weighed residue.

If the residue is white, calculate the percentage of silicon in the sample.

If, as sometimes happens, the silica is not quite white, add a few drops of hydrofluoric acid to the contents of the weighed platinum capsule (this must not be done in a porcelain capsule or crucible), carefully evaporate, ignite, allow to cool in a desiccator, and re-weigh.

The percentage of silicon in silica is 47·02, and when 2 grammes of sample are taken for the estimation, the factor for calculating the percentage is—

$$\frac{47·02}{2} = 23·51.$$

Log 23·51 = 1·3712526.

EXAMPLES.—

(a) Without the use of hydrofluoric acid.

		Grammes.
Weight of capsule + silica + ash	=	19·1458
„ capsule	=	19·0685
„ silica + ash	=	0·0773
„ filter ash	=	0·0008
„ silica	=	0·0765

$$0·0765 \times 23·51 = 1·799.$$

1·80 ÷ percentage of silicon in the sample of pig iron.

(*b*) Using hydrofluoric acid.

	Grammes.
Weight of capsule + contents, . =	18·7243
Weight of capsule + impurities after treatment with hydro-fluoric acid . . . . =	18·6913
	0·0330
Add for impurity in the hydro-fluoric acid, the amount of which had been previously ascertained in a like quantity of the acid . =	0·0010
Weight of residue volatilised = *silica* . . . . . =	0·0340

Then using the factor (23·51) noted in example (*a*),

$$0\cdot034 \times 23\cdot51 = 0\cdot799.$$

0·80 = percentage of silicon in the sample of white pig iron.

ESTIMATION OF PHOSPHORUS IN PIG IRON.

STANDARD METHOD—APPLICABLE TO ALL PIG
IRONS EXCEPT SWEDISH AND HEMATITE.

Outline of the Process.—The weighed sample
is treated with acid, evaporated to dryness, and
baked.   On boiling the residue with acid, all the
usual components of ordinary pig iron, except
graphitic carbon and silicon, are dissolved and are
separated from the insoluble residue (which may
be used to ascertain the percentage of silicon) by
filtering and washing.   To the filtrate, molybdate
solution is added to cause the precipitation of a yellow
compound $[(NH_4)_3PO_4 . 12MoO_3]$ containing all the
phosphorus. The yellow precipitate is collected on
a filter and washed, thus separating the phosphorus
from the iron. The washed precipitate is dissolved
in ammonia liquor and the solution is neutralised.
Magnesia mixture is then added to precipitate the phos-
phorus as magnesium-ammonium-phosphate, which is
collected, washed, and dried. On ignition it is con-
verted into magnesium pyrophosphate $(Mg_2P_2O_7)$ which
is weighed. From the weight of the precipitate the
percentage of phosphorus in the steel is calculated.

Details of the Process.—Weigh off 2 grammes
of the sample.

Transfer the weighed portion to a 12·2 × 9·6 cm.
(about $4\frac{3}{4} \times 3\frac{3}{4}$ inches) Bohemian or Jena beaker.

Add 15 c.c. of hydrochloric acid of 1·16 specific gravity along with 15 c.c. of nitric acid.

Evaporate on a hot plate to dryness (see note on hot plate, p. 377), then allow to stand on the hot plate for ten minutes more to complete the oxidation of the phosphorus to phosphoric anhydride (P_2O_5).

Withdraw the beaker and place it on a cork mat.

When the beaker is not likely to crack in contact with liquid add 20 c.c. of hydrochloric acid and evaporate to about half bulk.

Add about 20 c.c. of hot water, and boil for two minutes.

Filter through a 12·5 cm. Swedish filter-paper, collecting the filtrate (and washings) in a 300 c.c. (about 10-oz.) conical flask.

Wash three times with dilute hydrochloric acid— 1 of 1·16 specific gravity acid to 6 of water.

Wash with warm water until all traces of colour are removed from the filter-paper and the washings are colourless. **Silicon may be estimated in the residue.**

While stirring the filtrate, add ammonia solution to it until a permanent precipitate forms.

Dissolve the precipitate by cautiously adding nitric acid while stirring.

Add 35 c.c. of ammonium-nitrate solution (see p. 402).

Heat to 90° C. Immediately raise the thermometer about 25 mm. (about 1 inch) clear of the solution and pour, all at once, 175 c.c. of molybdate solution (see p. 402) down the thermometer into the flask.

> **175 c.c. should be sufficient for a pig iron containing 3 per cent. of phosphorus. For a forge or foundry pig iron 100 c.c. should be enough.**

This will cause the formation of a yellow precipitate containing all the phosphorus.

Shake the flask well, and allow the precipitate to settle.

Filter the solution through a 12·5 cm. close-texture filter-paper, collecting the filtrate (and washings) in a beaker.

Wash, once by decantation and afterwards in the usual way, with nitric acid solution—1 of acid (specific gravity, 1·42) to 20 of water.

Remove the beaker containing the filtrate, and place in its stead a clean 500 c.c. beaker.

Dissolve the precipitate on the filter with dilute ammonia solution—1 of ammonia liquor (·880 specific gravity) to 8 of water—collecting the solution in the beaker.

Wash four times with dilute ammonia solution and twice with warm water. Collect the washings in the same beaker as the solution. Heat the solution and washings to about 60° C.

Add one-sixth bulk of ammonia liquor (0·88 specific gravity).

Add 25 c.c. of magnesia mixture (see p. 408), and stir well.

Allow the precipitate to settle.

Filter, using a 12·5 cm. Swedish filter-paper.

Wash with dilute ammonia solution—1 of am-

monia liquor (specific gravity, 0·88) to 8 of water—until the washings are free from chlorides.

Dry the precipitate by placing the funnel, with filter-paper and contents, on a filter dryer (Fig. 4, p. 14), covering with paper, and allowing to dry on the hot plate.

Place the dried residue and filter-paper in a tared platinum or porcelain capsule or crucible, and ignite.

The precipitate and filter should be thoroughly dried, and the ignition cautiously begun, so as to avoid highly heating the precipitate before the organic part of the filter is burnt away. The residue should be white (not grey) before removing the capsule to the hottest part of the muffle, where it should remain for an hour. Unless this is done, there is danger of the precipitate so clinging to the filter-paper that it becomes impossible to burn off the paper. During ignition, the precipitate loses ammonia and water, and is converted into magnesium pyrophosphate ($Mg_2P_2O_7$), thus—

$$2Mg(NH_4)PO_4 \cdot 6H_2O = Mg_2P_2O_7 + 2NH_3 + 7H_2O.$$

Withdraw the capsule, or crucible, and its contents and allow to cool in a desiccator.

Weigh, and note the weight.

The percentage of phosphorus is calculated from the weight of magnesium pyrophosphate, which contains 27·838 per cent. of phosphorus. When 2 grammes of sample have been operated on the factor for calculation is—

$$\frac{27 \cdot 838}{2} = 13 \cdot 919.$$

$$\text{Log } 13 \cdot 919 = 1 \cdot 1436080.$$

EXAMPLE—

		Grammes.
Weight of precipitate + filter ash + capsule =	19·9607
„ capsule	=	19·7385
„ precipitate + ash	=	0·2222
„ ash	=	0·0008
„ precipitate	=	0·2214

$$0·2214 \times 13·919 = 3·08.$$

3·08 = percentage of phosphorus in the sample of pig iron.

ESTIMATION OF PHOSPHORUS IN PIG IRON.

RAPID METHOD—NOT APPLICABLE TO SWEDISH OR HEMATITE PIG IRONS.

Outline of the Process.—The weighed sample is treated with acid, evaporated to dryness, and baked. On boiling the residue with acid, all the usual components of ordinary pig iron — except graphitic carbon and silicon—are dissolved, and are separated from the insoluble residue by filtering and washing. The filtrate and washings are collected in a 250 c.c. flask, cooled, and made up to definite volume. A measured quantity of solution is withdrawn by a pipette, and transferred to a flask. Ammonium nitrate is added to facilitate precipitation, and the whole is heated to a suitable temperature for precipitation by ammonium molybdate. The precipitate, which contains all the phosphorus in the

measured quantity, is collected, washed, dried, and weighed.

Details of the Process.—Weigh off 2 grammes of the sample in the form of drillings or fine turnings.

Transfer the weighed portion to a 12·2 × 9·6 cm. (about 4¾ × 3¾ inches) Bohemian or Jena beaker.

Add 15 c.c. of hydrochloric acid of 1·16 specific gravity along with 15 c.c. of nitric acid.

Evaporate on a hot plate (see p. 377) to dryness, then allow to stand on the hot plate for ten minutes more to complete the oxidation of the phosphorus to phosphoric anhydride (P_2O_5).

Withdraw the beaker and place it on a cork mat.

When the beaker is not likely to crack on contact with liquid, add 20 c.c. of 1·16 specific gravity hydrochloric acid, and evaporate to about half bulk.

Add 25 c.c. of hot water, and boil for two minutes.

If it is desired to estimate silicon in the washed residue:—

Filter through a 12·5 cm. Swedish filter-paper, collecting the filtrate and washings in a 250 c.c. flask.

Wash three times with dilute hydrochloric acid, say 1 of 1·16 specific gravity acid to 6 of water.

Wash with warm water until all traces of colour are removed from the filter-paper, and the washings are colourless. With ordinary care the residue can be completely washed without making the volume more than 250 c.c.

Cool the solution, make up to the mark with cold water, and mix well.

If it is not desired to estimate silicon in the washed residue :—

Wash the solution out of the beaker (without filtering) into a 250 c.c. flask.

Cool under a water tap.

Make up to the mark with cold water.

Mix well and allow to settle.

Withdraw from the clear portion of the solution, by means of a pipette, the quantity required for the phosphorus estimation ; or, if the results are required earlier, the measured portion from the pipette may be run through a filter and washed into the precipitating flask.

In either case—

Draw from the 250 c.c. flask enough of the solution to fill the pipette to the mark indicating the quantity which will deliver 20·38 c.c.   This is done to clean it. Reject the solution as it runs out.

Draw from the 250 c.c. flask more of the solution into the pipette, and adjust it to the 20·38 c.c. delivery mark.

Run the measured quantity into a 200 c.c. (about 7 ozs.) conical flask.

Add 2 c.c. of ammonia liquor.

Neutralise with hydrochloric acid.

Add 17 c.c. of ammonium nitrate solution (see p. 402).

Heat to 90° C.   Immediately raise the thermo-meter about 25 mm. (about 1 inch) clear of the solution, and add all at once 20 c.c. of molybdate solution (see p.402),which may be poured down the

lower part of the thermometer into the flask. This will cause the formation of a yellow precipitate containing all the phosphorus.

Withdraw the thermometer, cork the flask, and shake it vigorously for one minute or more. While shaking, press the forefinger on the cork to prevent its ejection.

Pour the solution with the yellow precipitate on to a 9 cm. close-texture, smooth-surface filter-paper. Wash any remaining precipitate on to the filter.

Wash the precipitate three times with very dilute nitric acid—1 of 1·42 specific gravity acid to 50 of water.

Open out the filter-paper, and, with a fine-spout wash bottle containing warm water, wash the precipitate into a tared porcelain basin or a tared basin of platinised nickel (see note on p. 378).

Evaporate on a water bath (Fig. 6, p. 21) till the precipitate is completely dried.

Wipe the basin and allow it to cool.

Weigh, and calculate the result.

Other plans are (a) to use counterpoised filter-papers, and (b) to brush the dried precipitate on to a tared watchglass, and weigh.

The yellow precipitate, when thoroughly dried on a water bath, contains 1·63 per cent. of phosphorus.

When the solution from 2 grammes is made up to 250 c.c., 20·38 c.c. = 0·163 gramme, and when this

quantity has been used for the estimation, the factor for calculation is

$$\frac{1\cdot 63}{0\cdot 163} = 10.$$

EXAMPLE—   Grammes.

Weight of basin + precipitate   .   = 24·669

     „   basin.   .   .   .   = 24·568

     „   precipitate,   .   .   =   0·101

$$0\cdot 101 \times 10 = 1\cdot 01.$$

1·01 = percentage of phosphorus in the sample of pig iron.

STANDARD METHOD FOR THE ESTIMATION OF PHOSPHORUS IN HEMATITE OR SWEDISH PIG IRONS.

MOLYBDATE AND MAGNESIA METHOD.

Outline of the Process.—The weighed sample is treated with acid, evaporated to dryness, and baked. On boiling the residue with acid, all the usual components of ordinary pig iron, except graphitic carbon and silicon, are dissolved and are separated from the insoluble residue (which may be used to ascertain the percentage of silicon) by filtering and washing. To the filtrate, molybdate solution is added to cause the precipitation of a yellow compound $[(NH_4)_3PO_4 \cdot 12MoO_3]$ containing all the phosphorus. The yellow precipitate is collected on a filter and washed, thus separating the phosphorus from the iron. The washed precipitate is dissolved in ammonia liquor and the solution is neutralised. Magnesia mixture is then added to precipitate the phosphorus as

magnesium-ammonium-phosphate, which is collected, washed, and dried. On ignition it is converted into magnesium pyrophosphate ($Mg_2P_2O_7$) which is weighed. From the weight of the precipitate the percentage of phosphorus in the steel is calculated.

Details of the Process.—Weigh off 5 grammes of the sample.

Transfer the weighed portion to a $15 \times 11 \cdot 5$ cm. (about $6 \times 4\frac{1}{2}$ inches) Bohemian or Jena beaker.

Add 40 c.c. of $1 \cdot 16$ specific gravity hydrochloric acid along with 20 c.c. of $1 \cdot 42$ specific gravity nitric acid.

Evaporate on a hot plate to dryness (see note on hot plate, p. 377).

Allow the beaker to stand on the hot plate for ten minutes more, to complete the oxidation of the phosphorus to phosphoric anhydride (P_2O_5).

Withdraw the beaker and place it on a cork mat.

When the beaker is not likely to crack in contact with liquid, add 35 c.c. of $1 \cdot 16$ specific gravity hydrochloric acid and allow to boil until all the iron appears to be dissolved.

Add about 20 c.c. of hot water, and boil briskly for a few minutes more.

Filter through a $12 \cdot 5$ cm. Swedish filter-paper, collecting the filtrate (and washings) in a 250 c.c. conical flask.

Wash three times with dilute hydrochloric acid— 1 of $1 \cdot 16$ specific gravity acid to 6 of water.

Wash with warm water until all traces of colour are removed from the filter-paper and the washings are colourless. **Silicon may be estimated in the residue.**

While stirring the filtrate, add ammonia solution to it until a permanent precipitate forms.

Dissolve the precipitate by cautiously adding nitric acid while stirring.

Add 35 c.c. of ammonium nitrate solution (see p. 402).

Heat to 90° C. Immediately raise the thermometer about 25 mm. (about 1 inch) clear of the solution, and pour down the stem of the thermometer, all at once, 33 c.c. of molybdate solution (see p. 402) into the flask. This will cause the formation of a yellow precipitate containing all the phosphorus.

Cork the flask and shake it vigorously, so as to hasten the precipitation.

Allow to settle at a temperature under 100° C. for about fifteen minutes.

Pour the solution with the yellow precipitate into a 9 cm. close-texture filter, collecting the filtrate (and washings) in a beaker. Wash the remaining precipitate into the filter.

Wash the precipitate three times with very dilute nitric acid—1 of 1·42 specific gravity nitric acid to 50 of water.

Remove the beaker containing the filtrate, and place in its stead a clean 300 c.c. conical flask.

Dissolve the precipitate on the filter with dilute ammonia solution—1 of ammonia liquor (0·88 specific gravity) to 8 of water—collecting the solution (and washings) in the conical flask.

Wash four times with dilute ammonia liquor, and twice with warm water.

Heat the solution and washings to about 60° C.

Add 10 c.c. of 0·88 specific gravity ammonia liquor. Mix the solutions in the flask.

Add, drop by drop, about 5 c.c. of magnesia mixture (see p. 408). Stir the solution briskly, or agitate the flask, while adding the magnesia mixture.

Cork the flask and shake it vigorously for about two minutes. (While shaking the flask, press the cork firmly to prevent its ejection.) This causes the formation of a finely crystalline precipitate of magnesium-ammonium-phosphate ($Mg(NH_4)PO_4 \cdot 6H_2O$).

Allow the precipitate to settle for an hour or two.

Decant the clear solution through a 12·5 c.m. Swedish filter, and with dilute ammonia liquor wash the precipitate into the filter. Collect the filtrate (and washings) in a suitable beaker.

Wash six times with dilute ammonia liquor.

Test the last washings with acidulated silver nitrate (see p. 381).

Wash two or three times with the dilute ammonia liquor after all the chlorides have been washed out.

Dry the precipitate by placing the funnel, with filter-paper and contents, on a filter dryer (Fig. 4, p. 14), covering with paper, and allowing to dry on the hot plate.

Place the dried residue and filter-paper in a tared platinum or porcelain capsule or crucible, and ignite.

The precipitate and filter should be thoroughly dried, and the ignition cautiously begun, so as to avoid highly heating the precipitate before the organic part of the filter is burnt away. The precipitate should be white (not grey) before removing the capsule to the hottest part of the muffle, where it should remain for

an hour. Unless this is done, there is danger of the precipitate so clinging to the filter-paper that it becomes impossible to burn off the paper. During ignition the precipitate loses water and is converted into magnesium pyrophosphate $= (Mg_2P_2O_7)$.

$$2Mg(NH_4)PO_4 \cdot 6H_2O = Mg_2P_2O_7 + 2NH_3 + 7H_2O.$$

Withdraw the capsule or crucible and allow to cool in a desiccator.

Weigh, and calculate the result.

The percentage of phosphorus is calculated from the weight of magnesium pyrophosphate, which contains $27 \cdot 838$ per cent. of phosphorus.

When 5 grammes of sample are used for the estimation, the factor for ascertaining the percentage is

$$\frac{27 \cdot 838}{5} = 5 \cdot 568.$$

Log $5 \cdot 568 = 1 \cdot 7456992$.

EXAMPLE—

		Grammes.
Weight of capsule + ash + precipitate =		$18 \cdot 3536$
,, capsule . . . . =		$18 \cdot 3472$
,, ash and precipitate . . =		$0 \cdot 0064$
,, filter ash . . . . =		$0 \cdot 0008$
,, precipitate ($Mg_2P_2O_7$) . =		$0 \cdot 0056$

$$0 \cdot 0056 \times 5 \cdot 568 = 0 \cdot 0312.$$

$0 \cdot 0312 =$ percentage of phosphorus in the sample of steel.

Rapid (Molybdate) Method for the Estimation of Phosphorus in Hematite or Swedish Pig Irons.

Outline of the Process.—The weighed sample is treated with acid, evaporated to dryness, and baked. On boiling the residue with acid, all the usual components of ordinary pig iron — except graphitic carbon and silicon—are dissolved, and are separated from the insoluble residue by filtering and washing. The filtrate and washings àre collected and evaporated to small bulk. Ammonium nitrate is added to facilitate precipitation, and the whole is heated to a suitable temperature for precipitation by ammonium molybdate. The precipitate, which contains all the phosphorus in the measured quantity, is collected, washed, dried, cooled, and weighed.

In estimating phosphorus by this method, regard must be paid to the quantity, the degree of acidity, and the temperature of the solution when precipitating. The amount of ammonium nitrate in the solution has also an effect on the precipitation.

Details of the Process.—Weigh off 5 grammes of the sample.

Transfer the weighed portion to a 15 × 11·5 cm. (about 6 × 4½ inches) Bohemian or Jena beaker.

Add 40 c.c. of 1·16 specific gravity hydrochloric acid along with 20 c.c. of 1·42 specific gravity nitric acid.

Evaporate on a hot plate to dryness (see note on hot plate, p. 377).

Allow the beaker to stand on the hot plate for ten minutes more, to complete the oxidation of the phosphorus to phosphoric anhydride (P_2O_5).

Withdraw the beaker and place it on a cork mat.

When the beaker is not likely to crack in contact with liquid, add 35 c.c. of 1·16 specific gravity hydrochloric acid.

Boil until all the iron appears to be dissolved.

Add about 10 c.c. of hot water, and continue the boiling for about two minutes.

Allow the residue to subside, and pour the clear yellow liquid through a 12·5 cm. Swedish filter, collecting the filtrate (and washings) in a $9 \times 7·5$ cm. (about $3\frac{1}{2} \times 3$ inches) Bohemian or Jena beaker.

Wash the residue into the filter.

Wash three times with water acidulated with 10 per cent. of 1·16 specific gravity hydrochloric acid.

Evaporate till the liquid is of the smallest possible bulk. If evaporation has been continued till some of the solution has dried on the glass, withdraw the beaker, and, when it has slightly cooled, gently pour one or more drops of hydrochloric acid on the spot, to dissolve the solidified matter. The beaker will then contain a concentrated and nearly neutral solution or syrup.

With a fine-spout wash-bottle containing warm water, wash the solution into a 150 c.c. (about 5-oz.) conical (Erlenmeyer) flask. Avoid dilution as much

as possible. The solution and washings should not measure more than 25 c.c.

Add 25 c.c. of ammonium nitrate solution (see p. 402).

Heat to about 90° C.

Immediately raise the thermometer about 2·5 cm. (about 1 inch) clear of the solution, and pour down the stem of the thermometer, all at once, 25 c.c. of molybdate solution (see p. 402) into the flask. This will cause the formation of a yellow precipitate containing the phosphorus.

Withdraw the thermometer, cork the flask, and shake it vigorously for about one minute. While shaking the flask, press the fore-finger on the cork to prevent its ejection.

Pour the solution with the yellow precipitate into a 9 cm. close-texture, smooth-surface filter-paper, collecting the filtrate (and washings) in a suitable beaker. Wash any remaining precipitate on the filter.

Wash the precipitate three times with very dilute nitric acid—1 of nitric acid (1·42 specific gravity) to 50 of water.

Open out the filter-paper, and, with a fine-spout wash-bottle containing warm water, wash the precipitate on to a tared porcelain basin or a basin of platinised nickel—see note on p. 378.

Evaporate on the water bath (Fig. 6, p. 21) till the precipitate is completely dried.

Wipe the basin and allow it to cool.

Weigh, and calculate the result.

The yellow precipitate, when thoroughly dried on

a water bath, contains 1·63 per cent. of phosphorus, and when 5 grammes of sample have been used for the estimation, the factor for calculation is

$$\frac{1·63}{5} = 0·326.$$

$$\text{Log } 0·326 = \overline{1}·5132176.$$

EXAMPLE—

Grammes.

Weight of basin + precipitate = 22·483

„   basin   .   .   . = 22·387

„   precipitate .   . = 0·096

$$0·096 \times 0·326 = 0·313.$$

$0·313 =$ percentage of phosphorus in the sample.

ESTIMATION OF MANGANESE IN PIG IRON.

GRAVIMETRIC METHOD.

Outline of the Process.—The weighed sample is treated with acid and evaporated to complete dryness. By this means the silicon is converted into insoluble silica. On the addition of more acid and the application of heat, the insoluble residue from an ordinary pig iron consists of silica and graphite only. The soluble portion is filtered off into a flask, and carefully neutralised. Ammonium acetate is added, and, on boiling, a bulky precipitate of ferric acetate and hydrate is formed. This is separated, by filtering and washing, from the liquid containing the manganese in solution. The manganese in the filtrate is peroxidised by the action of bromine.

On addition of ammonia, hydrated manganese oxide is precipitated. The precipitate is collected on a filter, washed, dried, and ignited. The percentage of manganese is calculated from the weight of the finished residue of Mn_3O_4.

Details of the Process.—Weigh off 2 grammes of the sample.

Transfer the weighed portion to a 12 cm. × 12 cm. (about $4\frac{1}{2}$ × $4\frac{1}{2}$ inches) Bohemian spouted beaker.

Add 15 c.c. of nitric acid, 1·42 specific gravity, along with 7 c.c. of hydrochloric acid of 1·16 specific gravity.

Evaporate on a hot plate till thoroughly dry (see note on hot plate, p. 378).

Withdraw the beaker and place it on a cork mat.

When the beaker is not likely to crack in contact with liquid, add about 20 c.c. of nitric acid along with 10 c.c. of water, and set to boil briskly for a few minutes.

Filter the solution through a 12·5 cm. Swedish filter, collecting the filtrate (and washings) in a 1,200 c.c. (about 40 ozs.) globular Bohemian flask.

Wash the residue (silica and graphite) three times at least with hot water.

Boil the filtrate and washings.

Add ammonia solution till a slight permanent precipitate forms and remains in the hot liquid, even after vigorous shaking. Much of the success of the estimation depends on the accuracy with which the neutralisation is effected.

Add about 600 c.c. of cold water.

Add 33 c.c. of ammonium acetate solution.

Then follow the details from the corresponding point on p. 35 to the end of the gravimetric process.

Estimation of Manganese in Pig Iron.

Colorimetric Method.

(From a Memo. by Percy Hill, Wednesbury.)

Outline of the Process.—When manganiferous pig iron in a fine state of division is dissolved in nitric acid, and silver nitrate and ammonium persulphate afterwards added, a pink colour appears, the depth of which depends on the amount of manganese present. The graphite and silica are allowed to settle, and a measured quantity of the clear pink-coloured solution is drawn off and transferred to a 50 c.c. Eggertz' tube. This is compared with the colour from an equal weight of pig iron containing a known percentage of manganese.

For pig irons containing under 1 per cent. of manganese, the colorimetric method for steels (see pp. 40 to 42) works satisfactorily if the graphite and silica are allowed to settle and 5 c.c. are drawn off for the estimation ; but, if like quantities of solutions are used for pig irons containing over that percentage of manganese, a precipitate will separate out. This precipitation is avoided if Percy Hill's modification is adopted.

Details of the Process.—Weigh 0·1 gramme of the sample, which must be fine enough to pass through a 100-mesh sieve.

Transfer the weighed portion to an 18 × 1·6 cm. (about 7 × ⅝ inch) test tube.

Weigh off an equal quantity of a suitable standard steel and transfer to a similar test tube.

Add 8 c.c. of nitric acid of 1·2 specific gravity to each.

Place the test tubes in a water bath (see p. 21), and allow them to remain until the iron has dissolved —generally about ten to fifteen minutes.

Add to each, 7·5 c.c. of 0·4 per cent. solution of silver nitrate.

Replace the test tubes with their contents in the water bath, and add to each about 1 gramme of previously moistened persulphate (see note on persulphate, p. 419).

Continue heating in the water bath until the colour appears, and, while the tubes are still effervescing, remove the tubes and place them in a cold-water bath.

When the solid residues in the tubes have subsided, draw off, with a pipette, 5 c.c. of the clear pink-coloured solution from the standard "pig" to a marked Eggertz' tube, make up with cold water to a suitable volume, and mix thoroughly.

Transfer a similar quantity of the coloured solution from the sample "pig" to a corresponding Eggertz' tube, dilute, and compare with the standard solution.

NOTE.—In comparing the tints, the graduated tubes are placed side by side, so that diffused light coming through the ground glass or a sheet of moistened filter-paper will pass through the solutions (see Fig. 2, and description of stand on pp. 5 and 6). Change the relative positions of

the tubes—standard tube to the right, and sample tube to the left, and *vice versâ*—during the comparison.

Dilute with cold distilled water as far as necessary, mix well, and compare again.

When the solutions in each tube agree in depth of colour, note the volumes, and calculate the percentage of manganese.

GENERAL RULE FOR CALCULATING.—Divide the percentage manganese of the standard pig iron by the volume of its solution, and multiply the result by the volume of the solution of the pig iron which is being tested.

EXAMPLE.—Standard pig iron contained 2·35 per cent. of manganese, and the measured portion of its pink-coloured solution was diluted to 23·5 c.c. A similar measure of the pink-coloured solution from the sample required to be diluted to 19·4 c.c.

$$\frac{2 \cdot 35}{23 \cdot 5} \times 19 \cdot 4 = 1 \cdot 94.$$

1·94 = percentage of manganese in the sample, as shown by colour test.

ESTIMATION OF SULPHUR IN PIG IRON.

EVOLUTION AND GRAVIMETRIC METHOD.

In ordinary pig iron, sulphur is estimated in the manner described for steels in previous pages.

Usually 5 grammes of the sample are taken, and a duplicate estimation is made on 4 or on 6 grammes.

But certain pig irons (notably white irons) do not yield all their sulphur by evolution when dissolved in hot hydrochloric acid. In such cases, M'Farlane & Gregory, of Frodingham,* adopt the following method:—

Weigh off 5 grammes of the sample.

Intimately mix the weighed portion with half a gramme of sulphur-free cream of tartar (potassium-hydrogen-tartrate, $C_4H_5KO_6$).

Wrap the mixture in filter-paper, and place in a crucible, cover the crucible, and place the whole in a muffle which is at a good red heat.

Allow to remain for about fifteen minutes, the muffle being kept at a red heat all the time.

Withdraw the crucible and contents, and, when cool, pound the mixture in a mortar, transfer to a 500 c.c. (about 17 ozs.) conical flask, and proceed with the estimation as detailed on pp. 43 to 54.

When there is occasion to suppose that all the

* See *Chemical News*, vol. xciii., p. 201.

sulphur has been evolved, take away the tube or flask through which the gases have been passed, and put another tube or flask with copper sulphate or cadmium sulphate solution in position, and continue the boiling for a few minutes. If a precipitate is formed, add it to that previously obtained. After experience has been gained, this precaution may be unnecessary.

ESTIMATION OF SULPHUR IN PIG IRON.

GRAVIMETRIC METHOD.

Outline of the Process.—A weighed quantity of the sample is treated with acids and with chlorate to dissolve the iron, &c., and to oxidise the sulphur and the silicon. The solution is evaporated to dryness; and more acid is added and evaporated. The dried mass is then boiled in acid, and the insoluble portion is separated by filtration. Barium chloride is added to the clear, hot filtrate. This causes the precipitation of barium sulphate—a reaction indicated by the equation,

$$K_2SO_4 + BaCl_2 = BaSO_4 + 2KCl.$$
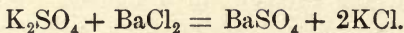
Barium sulphate is insoluble in the acid solution. It is collected on a filter, washed, dried, ignited, cooled, and weighed. The percentage of sulphur is then calculated.

Details of the Process.—Weigh off 5 grammes of the sample.

Transfer the weighed portion to a 13 × 10·5 cm. (about 5 × 4 inches) Bohemian or Jena beaker.

Add 40 c.c. of pure 1·16 specific gravity hydrochloric acid along with 20 c.c. of pure 1·42 specific gravity nitric acid, and heat gently.

When brisk action has ceased, add a few crystals of potassium chlorate, or the chlorate crystals may be previously dissolved in one of the acids.

Evaporate to dryness on a hot plate (see note on hot plate, p. 377), and allow to bake for twenty minutes after.

Withdraw the beaker and place it on a cork mat.

When the beaker is not likely to crack in contact with liquid, add 25 c.c. of pure 1·16 specific gravity hydrochloric acid, and again evaporate to dryness on the hot plate.

Again withdraw the beaker and place it on a cork mat.

When the beaker is not likely to crack in contact with liquid, add 40 c.c. of pure 1·16 specific gravity hydrochloric acid.

Boil, to dissolve the iron, &c.

Evaporate till a skin begins to form.

Withdraw the beaker and allow it to cool a little.

Add 5 c.c. of pure hydrochloric acid and about 20 c.c. of warm water.

Stir the solution well and immediately decant it into a 12·5 cm. Swedish filter, collecting the filtrate (and washings) in a 13 × 10·5 cm. (about 5 × 4 inches) Bohemian or Jena beaker.

Rinse the beaker twice with a little hot water

Decant the liquid into the filter.

Allow the whole to drain into the beaker.

Wash the filter twice with water, and allow the washings to drain into the beaker. The solution and washings should not measure more than 75 c.c.

Remove the beaker and set it on the hot plate.

When the liquid boils, add, drop by drop, 6 c.c. of a 10 per cent. solution of barium chloride.

Place a clock-glass over the beaker and boil the contents briskly for a few minutes.

Place the beaker in a warm place to allow the precipitate to settle.

Decant the liquid into a 12·5 cm. Swedish filter, collecting the filtrate and washings in a clean beaker of suitable size.

Pour about 100 c.c. of hot water and 2 c.c. of hydrochloric acid into the beaker, and shake it so as to mix the liquid and the precipitate.

Allow to settle in a warm place.

Again decant into the filter.

Pour another 100 c.c. of water into the beaker, and shake it so as to mix as before.

Drain the liquid and precipitate into the filter.

Wash several times with water.

Test the last washings with acidulated silver nitrate solution (see p. 381).

Wash twice with water after all chlorides appear to have been washed out.

Place the funnel, with filter-paper and contents, on a filter dryer (Fig. 4, p. 14) on a hot plate, and allow to remain till dried.

Place the dried residue and filter-paper in a tared platinum or porcelain crucible or capsule.

Ignite in a hot muffle.

Withdraw the crucible, or capsule, and contents, and place in a desiccator to cool.

Weigh, deduct the weight of the filter ash and the weight of barium sulphate in the blank, and calculate the percentage.

The weight of barium sulphate due to impurity in the acids used should be ascertained by a blank estimation, and deducted.

The blank estimation may be made on a mixture of 110 c.c. of the hydrochloric acid and 20 c.c. of the nitric acid. These should be evaporated to small bulk, cautiously diluted with water, boiled, barium chloride solution added, and set aside for twelve hours at least to complete precipitation. The precipitate is collected on a filter, washed, dried, ignited, and weighed. The Winchesters containing the acids should be labelled, and set aside for sulphur estimations only.

It is assumed that the water used does not contain sulphates. If this is not so, a measured quantity of the water, equal to the quantity used for an ordinary estimation, must be included in the blank estimation.

As the amount of the precipitated sulphate in the acids and chlorate is usually very small, precipitation takes place very slowly. To ascertain more quickly, and probably more accurately, the weight of the sulphate due to these, two weighed quantities of a sample of pig iron may be treated with like

quantities of the acids and chlorate, and the barium sulphate estimated by the method detailed above.

An example may make this point more clear :—

Let "blank" represent the $BaSO_4$ from the acids and chlorate used.

Weight of $BaSO_4$ from $7\frac{1}{2}$ grammes
   + blank   .   .   .   . = 0·0475 gramme.
Weight of $BaSO_4$ from $2\frac{1}{2}$ grammes
   + blank   .   .   .   . = 0·0225   „

            0·0250   „

The blank is the same in both cases, since equal quantities of acid and chlorate are used for each. The difference (0·025 gramme), therefore, shows the weight of $BaSO_4$ from 5 grammes of the sample.

$BaSO_4$ from 5 grammes   .   . = 0·0250 gramme.
   „ $7\frac{1}{2}$ „   = 0·025 × $\frac{3}{2}$ = 0·0375   „

$BaSO_4$ from $7\frac{1}{2}$ grammes + blank = 0·0475 gramme.
   „ $7\frac{1}{2}$ „   .   . = 0·0375   „

∴   „   blank   .   .   . = 0·0100   „

$BaSO_4$ from 5 grammes   .   . = 0·0250 gramme.
   „ $2\frac{1}{2}$ „   = 0·025 × $\frac{1}{2}$ = 0·0125   „

$BaSO_4$ from $2\frac{1}{2}$ grammes + blank = 0·0225 gramme.
   „ $2\frac{1}{2}$ „   .   . = 0·0125   „

∴   „   blank   .   .   . = 0·0100   „

Pure $BaSO_4$ contains 13·73 per cent. of sulphur, and, when 5 grammes are taken for analysis, the factor for ascertaining the percentage is

$$\frac{13\cdot73}{5} = 2\cdot746.$$

Log 2·746 = 0·4387005.

EXAMPLE—

Weight of crucible + ash and				
	blank + precipitate	=	17·4607	grammes.
„	crucible . . .	=	17·4428	„
„	ash + precipitate .	=	0·0179	„
„	filter ash + blank .	=	0·0013	„
„	precipitate ($BaSO_4$)	=	0·0166	„

$$0\cdot0166 \times 2\cdot746 = 0\cdot046.$$

0·046 = percentage of sulphur in the sample of pig iron.

ESTIMATION OF CARBON BY COMBUSTION.

DIRECT COMBUSTION OF THIN TURNINGS OR DRILLINGS OF STEEL.

Outline of the Process.—A weighed quantity of the sample, in the form of turnings or drillings not more than 0·25 mm. thick, is placed in a suitable boat in a porcelain tube set on a combustion furnace. The tube is brought to a bright red heat, and arrangements are made for the delivery of a steady supply of dry, pure air or oxygen. The constituents of the steel are oxidised, and the gases resulting from the oxidation of the carbon are carried forward—care being taken to convert all the carbon into dioxide—and absorbed in a solution of potassium hydrate in a Geissler's or Mohr's absorption bulb. The charged bulb is weighed before and after the combustion. From the increase in weight, due to the carbon dioxide absorbed, the percentage of carbon is calculated.

When oxygen is used the combustion is completed more rapidly than when air is employed. But oxygen is more liable to cause fusion and enclose a little of the carbon. Combustions conducted with air yield a slightly higher result. If precautions are taken to prevent access of moisture and impurities to the solution in the weighed absorption bulb, the higher result may be accepted as more accurate.

Apparatus Required.

(1) A combustion furnace. The kind shown in Fig. 9 is suitable.

This furnace, when made up of four blocks, makes a good support for the combustion tube, but only the central burners are required for carbon combustions.
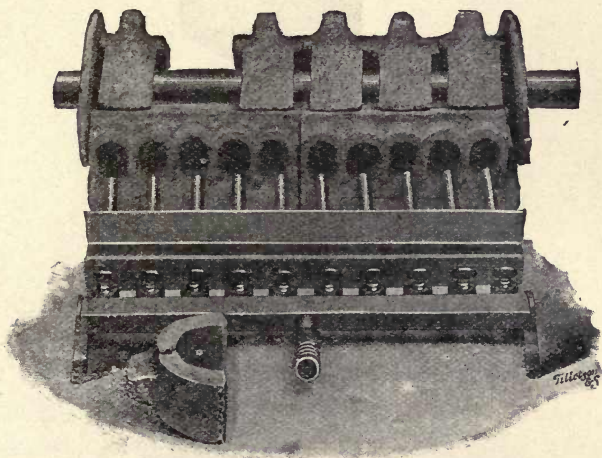
Fig. 9.—Combustion furnace.

(2) A Berzelius gasholder of 3 or 4 litres capacity (Fig. 10). Any other suitable gasholder may be used.

(3) A Dufty tower (Fig. 11) for purifying and drying the air.* The bottom portion is charged with about 200 c.c. of a strong solution of potas-

---

* See contribution by Lawrence Dufty, *Chemical News*, 19th June, 1903.

sium hydrate (caustic potash), and the upper part
is loosely packed with sticks of potassium hydrate
supported on the perforated plate.   On bubbling
air through the solution, carbon dioxide and other

Fig. 10.—Gasholder.

impurities are absorbed, and, on passing through
the chamber containing the solid potassium hy-
drate, the air is dried.

(4) A glass tower (Fig. 12) containing granular soda lime and fused granular calcium chloride. This is used to make sure that the air is thoroughly purified and dried.   The fused salts are supported on a piece of copper gauze placed at the constriction above the inlet.   The stopper may be turned so as to shut off air or prevent its passage.

Fig. 11.—Dufty tower.   Fig. 12.—Glass tower.

A U-tube with stopper-taps (Fig. 13) may be used instead of the tower.

(5) A porcelain combustion tube 26 inches long by $1\frac{1}{8}$ inch diameter, with an enlargement at each end for tight-fitting one-holed india-rubber

bungs. Only a small part of the tube requires to be heated, but a long tube is selected, so that the bungs will not be decomposed by the heat.

(6) An Arnold's absorption bulb, with the addition suggested by Dufty (Fig. 14). This is charged with about 15 c.c. of a nearly saturated solution of chromic acid in pure dilute sulphuric acid—water 9 : acid 11—and is intended to retain sulphur compounds.
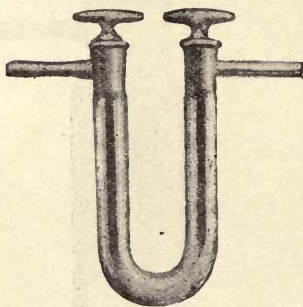
Fig. 13.—U-tube, with combined stoppers and taps
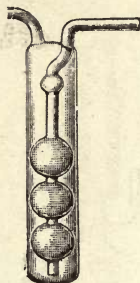
Fig. 14.—Arnold absorption bulb.

(7) A drying tower, same as No. 4 (Fig. 12), containing fused granular calcium chloride.

(8) A Mohr's or Geissler's absorption bulb (Fig. 15), each of the three lower bulbs of which is half-filled with a solution of potassium hydrate. This solution is made by dissolving 25 grammes of pure potassium hydrate in water, and making up with more water to 60 c.c.

The ground-on tube at the outlet end is charged with fused granular calcium chloride.

Potash solution is drawn into the bulbs by dipping the free end (B) into solution contained in a beaker and sucking from a rubber tube (with a glass mouthpiece) attached to the outlet (A). The inside of the inlet tube is then dried by means of a spill of filter-paper, and the remainder of the apparatus is wiped dry by a cloth which does not leave fluff on the glass.
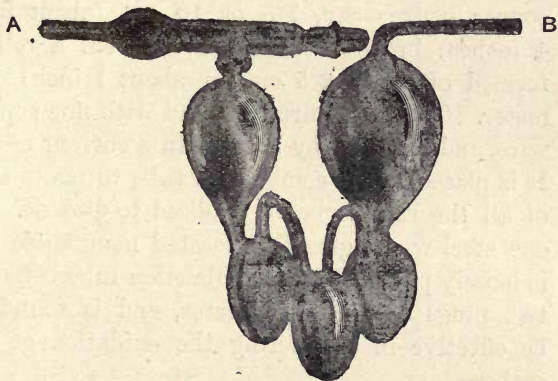
Fig. 15.—Bulb for absorption of carbon dioxide, with drying tube.

(9) A drying tower, same as No. 4 (Fig. 12), containing fused granular calcium chloride.

The several pieces (Nos. 2 to 9) are to be connected to each other by means of glass tubing (with ends fused round in a flame) and rubber tubing. The ends of the pieces of glass apparatus or the ends of the glass connections should be brought close to each other.

(10) Fireclay or magnesite combustion boats,

as made by the Morgan Crucible Co., Battersea Works, London. A stock of these boats should be highly heated in a good muffle furnace for two or three hours, and, when cooled a little, placed in a desiccator, and kept there till required.

(11) A roll of oxidised copper gauze. This is made by forming a loop at each end of a piece of stout copper wire and winding a length of copper gauze—say, 7·5 or 10 cm. (about 3 or 4 inches) broad—round the wire till a roll is formed of about 2·5 cm. (or about 1 inch) diameter. The roll is firmly bound with fine copper wire, and oxidised by heating in a current of air. It is placed in the combustion tube to make sure of all the carbon being oxidised to dioxide. In one steel work, granular roasted manganese ore is loosely packed in the combustion tube between two plugs of ignited asbestos, and is found to be effective in completing the oxidation of the carbon.

(12) A stout iron wire, about 2 feet long, bent at one end, and having a loop to indicate the distance to which the boats are to be pushed into the porcelain tube.

(13) Glass tubing for making connections.

(14) A number of good india-rubber junction or connecting pieces.

(15) A number of stoppers, made of small pieces of glass rod and india-rubber tubing. All ends of glass tubing and glass rod should be rounded in a flame.
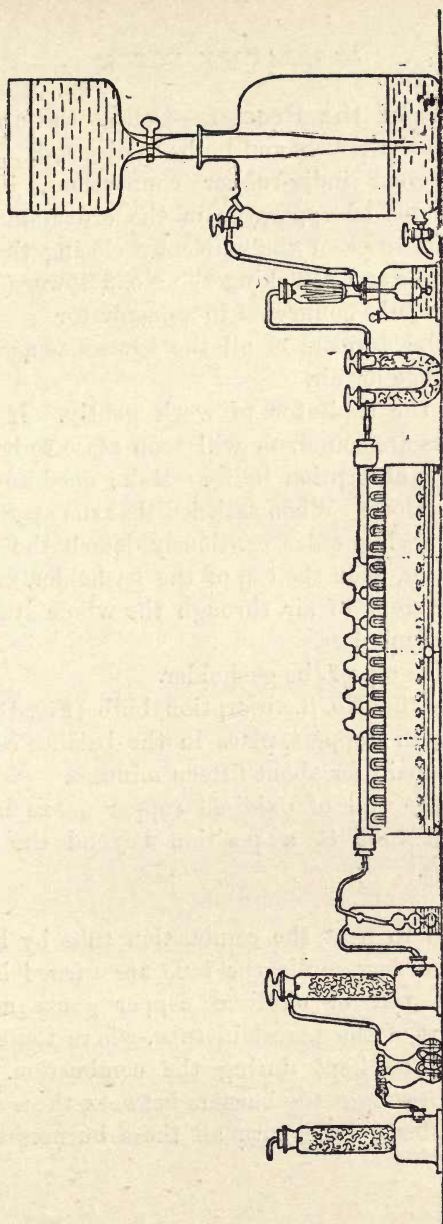
Fig. 16.—Arrangement of apparatus for carbon combustion.

Details of the Process.—Collect the apparatus and charge the towers and bulbs as directed.

With good india-rubber connections, join the various pieces of apparatus in the order stated, and test the tightness of the whole by closing the tap of the gasholder and attaching the No. 9 tower (Fig. 12) to a rubber tube connected to an aspirator.

Turn the stoppers of all the towers so as to leave a free passage for air.

Cause the aspirator to work gently. If all the connections are sound, air will soon cease to be drawn through the absorption bulbs. Make good any defective connections. When satisfied that the apparatus is in good working order, cautiously detach the tube to the aspirator, open the tap of the gasholder, and pass a gentle current of air through the whole system for about three minutes.

Close the tap of the gasholder.

Detach the No. 8 absorption bulb (Fig. 15), close the ends with stoppers, place in the balance case, and allow to remain for about fifteen minutes.

Push the roll of oxidised copper gauze into the combustion tube to a position beyond the middle of the tube.

Proceed to heat the combustion tube by lighting alternate burners, while the taps are turned half on, under the roll of oxidised copper gauze and the middle part of the porcelain tube, where the charged boat is to be kept during the combustion. After a few minutes light the burners between those already lit, and, after a time, turn all these burners full on,

and place the arched covering tiles over the hot part of the porcelain tube.

Weigh off 2·727 grammes of the sample of steel, which should be in the form of drillings or turnings in short pieces not more than 0·25 mm. thick.

Mix the weighed portion with well-burned powdered magnesite brick, and spread it in a combustion boat containing a thin layer of thoroughly calcined manganese ore.

Take the stoppers off the absorption bulb (Fig. 15), weigh, and note the weight.

Connect the weighed bulb with towers 7 and 9.

Place the charged boat in position in the hot combustion tube.

Press the india-rubber bung firmly into position.

Allow a current of air to issue from the gasholder, and pass through all the apparatus.

Maintain the furnace at a good red heat, and allow combustion to proceed for two hours.

Detach the No. 8 absorption bulb (Fig. 15) first from the No. 7 tower and then from the No. 9 tower, stopper the bulb, and place it in the balance case.

After about fifteen minutes take off the stoppers, again weigh the bulb with the absorbing solution, and note the weight.

Calculate the percentage of carbon.

EXAMPLE—

Weight of bulb, &c., after combustion,   43·7351 grms.
    „   „   before   „   43·7169   „

Weight of carbon dioxide absorbed, 0·0182   „

Percentage of C in CO_2 = 27·27.

$$\frac{27\cdot27}{2\cdot727} \times 0\cdot0182 = 0\cdot18.$$

0·18 = percentage of carbon in the sample.
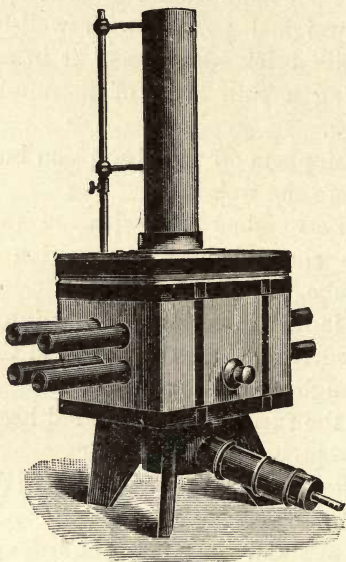
Fig. 17.—Huxley furnace.

If oxygen is used instead of air, the combustion may be completed in thirty minutes after action has begun. For a time no gas passes through the bulbs. as all the oxygen passed in combines to form carbon dioxide, which is all absorbed in the potash solution, When all the carbon has been oxidised, the oxygen bubbles through the Dufty tower and the weighed absorption bulb at the same rate.

To obtain reliable results by combustion practice is necessary. Even an analyst who has had experience in this class of work should make an estimation on a steel of known percentage of carbon before making an assay of an unknown sample—if he has been out of practice.

It is usual, where many estimations by combustion are regularly made, to keep four assays going simultaneously. For this purpose a Huxley tube furnace set on a Griffin's radial burner (Fig. 17) is used. The porcelain combustion tubes pass through the openings provided for that purpose. A cylindrical fireclay muffle surrounds the combustion tubes, so as to ensure uniformity of heating and obviate any fracture of the tubes. A central hole, used for lighting the burner is closed by a clay plug when the furnace is in use.

NOTES ON CARBON COMBUSTIONS.

For the estimation of carbon by combustion, the methods in use are :—

(1) Direct combustion, as described in the preceding pages.

(2) Direct combustion, as in (1), preceded by separation of the carbon.

(3) Moist oxidation, preceded by separation of the carbon, as in (2).

The direct combustion method, as detailed in the foregoing pages, is applicable to wrought iron, to all kinds of steel, to ferro-chrome, spiegel-eisen, ferro-manganese, &c., but cannot be depended on to yield good results when estimating the carbon in grey pig iron, silico-ferro, &c.

"When being burnt, theoretically every particle should be isolated from its fellow so that the oxygen in passing over the material may act on every side of them. In practice this is impossible, but a near approach to it can be effected by mixing the drillings with granulated particles of crushed magnesite brick or with granulated calcined manganese ore. When the drillings consist entirely of spiral pieces there is no need for any admixture whatever, as the oxygen can then act upon all parts without the intervention of any mechanical support. If, however, the particles of steel or metal are in fine powder, it is imperative that this mechanical suspension should be effected."— *Stead.*

In the hands of a competent analyst possessing

practical acquaintance with combustions, accurate and rapid results may be regularly obtained.

For the correct estimation of carbon in grey pig iron, ferro-silicon, &c., it is necessary that, prior to combustion, a residue containing all the carbon should be obtained. For this purpose the weighed sample is dissolved in an acidified solution of copper-potassium chloride, and the carbonaceous residue is collected on a filter of prepared asbestos fibres.

There is always an evolution of hydrocarbon gases during solution of steels, &c. This, of course, leads to the results being invariably low. The higher the percentage of carbon in a steel, the greater is the loss due to escaping hydrocarbons.

The same steel has been proved to yield a larger amount of hydrocarbon gases after hardening than was evolved in an unhardened state.* Hardened steels must therefore be annealed before being dissolved in acidified copper-potassium chloride.

* Dillner, *Iron and Steel Institute Journal,* vol. ii., 1904, p. 255.

Separation of Carbon for Estimation by Combustion.

Outline of the Process. — On dissolving a sample containing both combined and graphitic carbon with acid, the combined carbon is converted into hydrocarbons which escape in the gaseous state. This escape may be prevented by treating the sample with copper chloride solution. The copper precipitated while dissolving is more easily soluble in an acid solution of copper-potassium chloride.

The carbonaceous residue is collected and washed on a filter which is made by carefully packing a plug of prepared asbestos on the perforated disc of a Reinhardt funnel (Fig. 18). The finely - shredded asbestos is washed to get rid of chlorides, dried, and ignited before being packed in the funnel. A filter pump is used in connection with this.

Details of the Process. — Weigh off a portion of the sample, which should be in the form of shavings or in powder. These should neither be too fine nor too coarse. For ordinary pig iron 1·3635 gramme may be weighed off; a greater or lesser quantity should be taken for materials containing less or more carbon.

To 1·3635 gramme in an 11 × 11 cm. (about $4\frac{1}{2}$ × $4\frac{1}{2}$ inches) beaker, add 200 c.c. of an acidified solution of copper-potassium chloride (see p. 410).

Heat gently to promote circulation, stir frequently, and finally boil until solution of the iron is complete

and no trace of free copper remains. Blair hastens
solution by stirring the liquid by a machine.

When the precipitated copper is all, or very
nearly all, dissolved, run a little of the acidulated
double chloride around the inside of the beaker,
directing by means of the stirring rod, wash the rod
over the beaker with a jet of water, and let the
beaker stand for a few minutes to allow the car-
bonaceous matter to settle.

Fig. 18.—Reinhardt funnel for asbestos plug.

Collect this residue on the asbestos plug. Do not
allow the lip of the beaker to touch the surface of the
liquid in the plug, or a film of carbonaceous matter
will run up the inside of the beaker.

Wash several times with water containing a little
hydrochloric acid and some fine, ignited asbestos
fibres. The addition of the fibres, suggested by
Barba, promotes the settling of the carbonaceous
matter and prevents the clogging of the filter.

The carbonaceous residue from puddled iron, spiegel-eisen, ferro-manganese, and ingot steel usually washes like sand; but that from steel which has been hardened, tempered, hammered, or rolled is apt to be more or less gummy, stopping the filter and rendering the filtration long and tedious. It is also apt to adhere more or less to the sides of the beaker, and must be wiped off by a small wad of ignited, fibrous asbestos held in a pair of fine platinum - pointed forceps. This wad is then placed on the asbestos filter or plug.

Wash three or four times more, using pure distilled water.

Allow to drain well and then stop the action of the filter pump. Place a layer of prepared asbestos over the washed residue, so as to form a sandwich with the carbon, &c., in the centre.

Push the whole out of the funnel.

If intended for dry combustion, place in a hot-air bath, and, when dry, pack in a fireclay or magnesite boat, and proceed with the combustion as directed on pp. 105, 106.

If the carbon is to be oxidised by the wet process, continue the determination as directed on the next page.

Estimation of Carbon by Wet Oxidation.

Apparatus Required.

(1) A gasholder, as shown by Fig. 10, p. 100. This is used for testing the apparatus.

(2) A Dufty tower, as shown by Fig. 11, p. 101. This is charged as directed on pp. 99 and 100.

(3) A glass tower, as shown by Fig. 12, p. 101, containing granular soda lime and fused granular calcium chloride.

(4) A 250 c.c. conical flask with a tight-fitting two-hole rubber cork, carrying a funnel with stop-cock, and a delivery tube.

(5) An Argand burner, on which the conical flask is set.

To the delivery tube, the following, as used by Stead,[*] should be attached by rubber connecting pieces in the order named, viz. :—

A series of **U** tubes containing respectively anhydrous copper sulphate, cuprous chloride, chromic acid, and calcium chloride. To the last-named, the charged and weighed Geissler potash bulbs (Fig. 15, p. 103) are attached, and a **U** tube or tower containing granular calcined calcium chloride is connected to the outlet end of the bulb.

Connect the various parts in series.

Tare the charged Geissler bulbs and note the weight.

[*] *Iron and Steel Institute Journal,* vol. ii., 1904, p. 260.

Connect the bulbs, and test the efficiency of the system by drawing a current of dried and purified air through the whole series. Close the stopcock of the funnel and continue the aspiration. When satisfied that all the connections are tight, open the stopcock and draw dried and purified air through the whole system for a few minutes. Detach the Geissler bulb, wipe with a clean piece of silk, stopper the ends with glass rod and rubber pieces, and place the whole in the balance case. After about ten minutes, re-weigh. The weights should not show either increase or decrease.

When satisfied that all the apparatus is in good order, tare the Geissler bulb again (if necessary) and go on with the oxidation.

Transfer the still moist sandwich containing the carbonaceous residue to the 250 c.c. conical flask.

Add 15 c.c. of 50 per cent. chromic acid solution (see p. 404).

Press the cork carrying the stoppered funnel and delivery tube into the neck of the flask, and quickly make the necessary connections.

Measure 40 c.c. of 1·8 specific gravity sulphuric acid into the stoppered funnel.

Allow the acid to flow into the flask in small instalments, closing the tap between each.

Heat, gently at first, and later more strongly, until white fumes appear in the flask.

Detach the Geissler bulb, close the ends, wipe the bulb, place in the balance case, and allow to remain about fifteen minutes.

Take off the stoppers, and again weigh the bulb.

Calculate the percentage.

$$\frac{\left\{\begin{array}{c}\text{Weight of carbon dioxide}\\ \text{absorbed} \times 27 \cdot 27\end{array}\right\}}{\text{Weight of sample taken}} = \left\{\begin{array}{c}\text{percentage of carbon}\\ \text{in the sample.}\end{array}\right.$$

Knut A. Gunnar Dillner (Stockholm) introduces a platinum tube—which is kept red-hot during the oxidation—between the conical flask and the tube containing calcium chloride, which is placed before the Geissler bulb. The U tubes containing copper sulphate, cuprous chloride, and chromic acid are not required. The evolved gases are passed through the red-hot platinum tube, and very satisfactory results are obtained.

ESTIMATION OF CARBON IN PIG IRON, FERRO-SILICON, &c.

Graphitic carbon may be estimated by collecting the insoluble residue obtained as directed on pp. 13 and 14 on an asbestos filter (see p. 381). After washing, the residue—which consists of graphite and silica, with perhaps a little iron—is dried and placed in a Battersea fireclay or magnesite combustion boat, which is then pushed into a hot combustion tube. A high temperature is maintained to ensure the complete combustion of the graphite.

The apparatus is arranged as previously described, and all the customary precautions are taken.

The percentage is calculated from the weight of the carbon dioxide absorbed in the Geissler bulb.

ESTIMATION OF IRON.

VOLUMETRIC METHODS.

Frequently the amount of iron in a substance may be conveniently and accurately ascertained by a volumetric method. For this purpose the sample must be brought into solution under proper conditions. Standard solution of an oxidising agent is then added from a measuring apparatus, and, when the oxidation is complete, the measured volume of the standard solution is noted and the necessary calculations are made.

Towards the end of a reaction the standard solution is cautiously added drop by drop, and as the strength or power of the standard solutions are known, such volumetric estimations are known as titrations—from a French word, *titre*, signifying power or capacity.

The methods generally employed in the volumetric estimation of iron are :—

    (*a*) Marguerite's—the Permanganate method— and
    (*b*) Penny's—the Dichrome method.

Both methods are based on the amount of oxidising agent required to convert ferrous salt to ferric salt.

The dichrome method is generally preferred in British iron works.

In each case a weighed portion of the sample is dissolved in acid. If all the iron is not in the ferrous state it must be reduced—unless it is intended to estimate, separately, the ferrous and ferric iron—and any excess of reducing agent driven off or "corrected." The solution (reduced if necessary) is subjected to the selective, oxidising action of a standardised solution carefully measured from a burette. When the ferrous iron has all been oxidised, the quantity of standard solution used is read off and the necessary calculations made.

The state in which the iron exists in a solution is shown by **indicators,** thus—

A drop of acidified ferrous solution, when brought into contact with a drop of weak solution of ferri-cyanide (not ferrocyanide) of potash, yields a blue colouration or a blue precipitate.

A drop of acidified ferric solution, when brought into contact with a drop of alkaline sulpho-cyanide (thiocyanate of ammonia, potash, or soda) solution, shows a blood-red colour, or, if in very small quantity, a faint pink colour.

Convenient reducing agents are nascent hydrogen (from action of acid on zinc); sulphurous anhydride; and, for dichrome titration, **stannous chloride.**

ESTIMATION OF IRON BY TITRATING WITH A STANDARD SOLUTION OF POTASSIUM PERMANGANATE
$(K_2O \cdot Mn_2O_7)$.

The reaction which takes place on peroxidising ferrous iron may be represented thus:—

$$K_2O \cdot Mn_2O_7 + 10FeO, SO_3 + 8H_2SO_4$$
$$= 5Fe_2O_3, 3SO_3 + 2MnSO_4 + K_2SO_4 + 8H_2O.$$
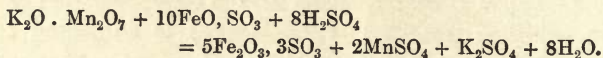
When all the iron has been oxidised to the ferric state further additions of potassium permanganate impart a pink colour to the liquid in the flask.

Quantity of potassium permanganate required for standard solution for the estimation of iron.

The molecular weight of potassium permanganate is 316·3.

316·3 grammes can peroxidise 55·9 × 10 grammes of ferrous iron, and

$$\frac{316 \cdot 3}{559} = 0 \cdot 56533.$$

or every gramme of iron requires 0·56583 gramme of permanganate.

If, therefore, 5·6583 grammes of potassium permanganate are dissolved and made up with water (at 15·5° C.) to 1 litre, every c.c. of the solution will equal 0·01 gramme of iron.

PREPARATION OF STANDARD SOLUTION OF PERMANGANATE FOR THE ESTIMATION OF IRON.

Pound in a mortar about 2 grammes of pure potassium permanganate. This will be a sufficient quantity for a student to experiment on.

Dry the pounded sample.

Weigh off 1·415 gramme of the salt. (The theoretical quantity required is 1·4146 gramme.)

Transfer the weighed quantity to a 400 c.c. beaker or beaker flask.

Add about 100 c.c. of warm distilled water.

With a glass rod (without rubber) stir well to hasten solution.

Pour some of the liquid into a 250 c.c. glass-stoppered graduated flask, taking care not to allow any undissolved salt to enter the flask.

Add more warm distilled water to the contents of the beaker.

Stir well, as before.

Pour off more of the solution into the flask.

Make sure that all the salt is dissolved.

Transfer the remainder of the solution to the graduated flask.

Make up nearly to the mark with cold water.

Bring the solution to 15·5° C. and make up to the mark with water at that temperature.

Stopper the flask and shake it briskly.

NOTE.—Once a standard solution is made up it must be kept carefully stoppered. If a quantity of standard

solution is made for stock, the containing bottle should have a label showing the strength of the solution and the date of standardising. Portions of the standard solution which have been taken out must not be returned to the bottle.

PREPARATION OF A SAMPLE OF MOHR'S SALT FOR STANDARDISING.

Mohr's salt is a compound sulphate of iron and ammonium $Fe(NH_4)_2(SO_4)_2$. $6H_2O$ and, when pure, contains 14·26 per cent., or nearly one-seventh its weight of ferrous iron. It may be purchased "chemically pure," or be prepared in the laboratory by the following method :—

Weigh off 27·8 grammes of pure recrystallised ferrous sulphate ($FeSO_4$. $7H_2O$).

Dissolve in minimum quantity of water at 40° C.

Weigh off 13·2 grammes of pure ammonium sulphate, $(NH_4)_2SO_4$.

Dissolve in minimum quantity of cold water.

Pour the ammonium sulphate solution into the solution of ferrous sulphate.

A granular precipitate of the double sulphate forms as the solution cools.

Wash by decantation.

Dry between the folds of bibulous paper under a press.

Preserve the dried sample in a clean, dry, stoppered bottle.

ARTICLES REQUIRED FOR STANDARDISING THE PERMANGANATE SOLUTION.

These articles should all be ready before beginning to standardise.

> A 30 or 50 c.c. burette, graduated in one-tenths ; burettes for permanganate solution must have glass stopcocks.
>
> An Erdmann's float.
>
> A burette stand.
>
> Three clean, dry, 10-oz. conical or globular flasks.
>
> The standard solution, and
>
> About 10 grammes of pure, dry Mohr's salt or a few grammes of pure iron wire.

STANDARDISING THE PERMANGANATE SOLUTION BY MOHR'S SALT.

Clean the burette, first with water and then with some of the standard permanganate solution.

Run off, into a sink, the permanganate solution used for cleaning the burette.

Fix the burette in the stand.

Nearly fill the burette with standard permanganate solution.

Put in the Erdmann's float and adjust to zero.

Weigh off accurately about 1·75 grammes of the Mohr's salt, and note the weight taken.

Transfer to a clean, dry 300 c.c. (about 10-oz.) conical or globular flask.

Add 100 c.c. of distilled water, to which about

5 c.c. of pure sulphuric acid has previously been added.

Shake the flask until the salt has dissolved.

Add standard permanganate solution from the burette to the solution in the flask as long as the colour readily disappears.

Set the flask on a white tile or piece of white paper when examining for the colour.

Continue to add standard permanganate solution cautiously, and with occasional shaking of the flask, until a faint permanent pink colour appears.

The reaction may be expressed by the equation—

$$K_2O \cdot Mn_2O_7 + 10FeO, SO_3 + 8H_2SO_4$$
$$= 5Fe_2O_3, 3SO_3 + 2MnSO_4 + K_2SO_4 + 8H_2O.$$
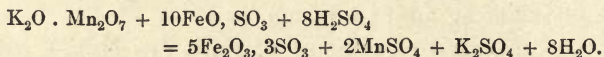
Read off and note the quantity of standard permanganate solution required to complete the reaction.

A little quantity of the permanganate solution is required to impart a pink tint to the solution in which the salt was dissolved   To allow for this a **blank experiment** should be made thus:—

Into a 300 c.c. (about 10-oz.) conical flask measure 100 c.c. of distilled water and 6 c.c. of pure sulphuric acid.

Note the amount of standard solution in the burette, and from it run two or three drops into the conical flask.

Shake the flask so as to mix the contents.

Compare the pink tint with that in the flask in which the iron estimation has just been made.

If necessary, add more standard permanganate to bring the liquid to the same depth of colour.

Note the quantity taken, and deduct from the amount noted as required to effect the oxidation of the iron solution.

Calculate the result.

EXAMPLE OF CALCULATION—

1·776 gramme of Mohr's salt required 25·30 c.c. of the standard permanganate solution, after making allowance for the blank colouration.

Iron in Mohr's salt, $\dfrac{1 \cdot 776 \times 14 \cdot 26}{100} = 0 \cdot 2533,$

$$\frac{0 \cdot 2533}{25 \cdot 30} = 0 \cdot 010012.$$

Every 1 c.c. of the standard permanganate solution = 0·010012 gramme of iron.

Experiments on 2·035 grammes and on 1·638 grammes, together with the result recorded above, showed that (on an average) every c.c. of the standard permanganate solution = 0·010011 gramme of iron.

EXERCISES IN THE ESTIMATION OF IRON BY MEANS OF STANDARD PERMANGANATE SOLUTION.

Clean a burette with distilled water and then with standard permanganate solution. Run off, into a sink, the permanganate solution used for cleaning the burette.

Fix the burette in a stand.

Nearly fill the burette with standard permanganate solution, put in an Erdmann's float, and adjust to zero.

Weigh off accurately about 2 grammes of pure, dry Mohr's salt, and note the weight taken.

Transfer the weighed quantity to a clean, dry 300 c.c. (about 10-oz.) conical or globular flask.

Add about 100 c.c. of water to which about 5 c.c. of sulphuric acid has been added.

Shake the flask until the salt has dissolved.

Add standard permanganate solution from the burette to the solution in the flask as long as the colour readily disappears.

Set the flask on a white tile, or a piece of white paper, when examining for colour.

Continue to add the standard permanganate solution cautiously, and with occasional shaking, until a faint pink colour is obtained which is permanent even after shaking the flask.

Read off, and note the quantity of standard solution required to complete the reaction.

Deduct the quantity required for blank.

Calculate the result.

EXAMPLE—

Weight of Mohr's salt taken = 2·0092 grammes. Standard permanganate solution required, less the quantity for blank = 28·61 c.c.

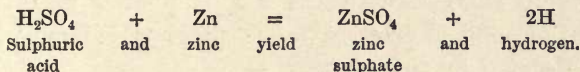Every c.c. = 0·010011 gramme of iron.

28·61 × 0·010011 = 0·2864 gramme.

0·2864 = weight of iron found in 2·0092 grammes of Mohr's salt.

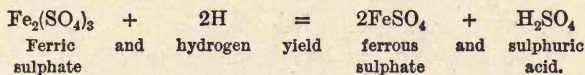$$\frac{0\cdot2864 \times 100}{2\cdot0092} = 14\cdot254$$

and 14·254 = percentage of iron found in Mohr's salt.

Having—by means of standard permanganate solution—oxidised the iron to the ferric state, the iron in the solution should now be *reduced* to the ferrous condition.

Reduction of ferric solutions may be effected by means of a reductor (see p. 388) or by adding granulated zinc, or small pieces of thin stick zinc and sulphuric acid. The zinc used for this purpose should be free from iron. The reaction between the zinc and acid gives rise to the evolution of hydrogen :—

$$H_2SO_4 \quad + \quad Zn \quad = \quad ZnSO_4 \quad + \quad 2H$$

Sulphuric   and   zinc   yield   zinc   and   hydrogen.
acid   sulphate

The zinc sulphate remains in solution, and takes no part in the work; the ferric salts are reduced to ferrous by the action of nascent hydrogen, thus :—

$$Fe_2(SO_4)_3 \quad + \quad 2H \quad = \quad 2FeSO_4 \quad + \quad H_2SO_4$$

Ferric   and   hydrogen   yield   ferrous   and   sulphuric
sulphate   sulphate   acid.

To ascertain if all the ferric iron has been reduced, bring a drop of the solution on the end of a stirring rod into contact with a drop of dilute thio-cyanate (sulphocyanide) solution on a white enamelled slab or a piece of drop-reaction paper. If more than a faint pink colour results, reduction is not complete.

Prof. M. M. Pattison Muir points out (*Chemical News*, 31st January, 1908) that if a small quantity of zinc is used for effecting reduction the action is slow, and if a large quantity of zinc is used time is lost in completing its solution. He suggests the addition of

saturated aqueous solution of mercuric chloride as soon as the reduction is finished. This stops the further action of acid on the remaining zinc, and allows the titration to be proceeded with at once. The author now uses mercuric sulphate in dilute sulphuric acid to stop the action of acid on the zinc. This he prefers to the usual practice of filtering through glass wool.

Sulphurous anhydride, as supplied in syphons, is very convenient for reducing ferric solutions. Water strongly charged with the gas is poured into the solution, and a reaction takes place which may be represented by the equation—

$$Fe_2O_3 \quad + \quad H_2O \quad + \quad SO_2 \quad = \quad 2FeO \quad + \quad H_2SO_4$$

Ferric and water and sulphurous yield ferrous and sulphuric
oxide   anhydride   oxide   acid.
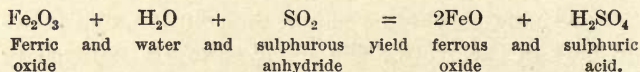
If sulphurous anhydride is used as the reducing agent, excess must be boiled off.

When the solution has been brought into proper condition, proceed with the titration as before. The result should correspond with the one previously obtained. If not, reduce again, and repeat the titration.

ESTIMATION OF IRON IN ORE BY MEANS OF STANDARD PERMANGANATE SOLUTION.

Before making an assay by titration, the student should practise the exercises set on the previous pages.

Collect the articles required (see p. 123).

Clean the burette, first with water, and then with some of the standard permanganate solution. Run

off, into a sink, the permanganate solution used for cleaning the burette.

Fix the burette in a stand.

Nearly fill the burette with standard permanganate solution. This solution should, after two or three weeks, be restandardised before using.

Place an Erdmann's float in the solution in the burette.

Adjust the float to zero.

The ore, having been carefully sampled, and the sample pounded, well mixed, bottled, and labelled, a portion should be withdrawn for assaying. This portion should be finely pounded in an agate mortar.

Weigh off accurately 1 gramme of the finely-powdered ore.

Place the weighed portion in a 300 c.c. (about 10 ozs.) conical flask.

Add about 100 c.c. of dilute sulphuric acid (6 vols. of acid to 100 of water).

Put a funnel in the neck of the flask, and set on a hot plate so as to hasten solution.

When all the iron has dissolved, remove the flask, wash the condensed liquid on the funnel into the flask, and reduce the ferric oxide as directed on p. 127.

Proceed to titrate as directed on p. 124.

Note the quantity of standard solution taken, and deduct the blank.

Calculate the percentage (see example on p. 126).

If ferrous and ferric oxides are required, proceed as directed on p. 139.
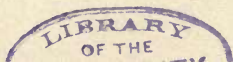
Estimation of Iron by Titrating with a Standard Solution of Potassium Dichromate ($K_2Cr_2O_7$ or $K_2O . 2CrO_3$).
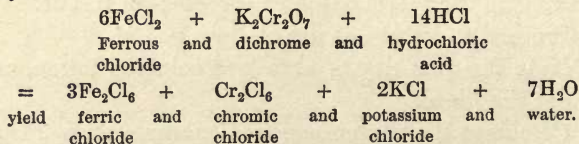
This orange - coloured salt (commonly called "bichrome") can be readily obtained in a fair state of purity, and its solution, if properly kept, remains constant in strength for a long time : it is practically permanent. Under easily-established conditions it parts with oxygen to ferrous oxide (FeO), converting it into ferric oxide (Fe_2O_3).

By measuring the amount of standardised dichrome solution required to effect the change, the amount of iron which was present in the ferrous state can be ascertained.

The chemical changes which take place when iron is dissolved in hydrochloric acid may be expressed by the following equation :—

$$Fe + 2HCl = FeCl_2* + H_2$$

Iron and hydrochloric yield ferrous and hydrogen.
acid chloride
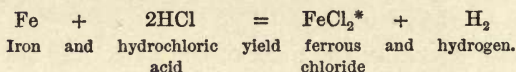
On adding dichrome solution the ferrous chloride is acted on, and the chemical reactions which occur may be indicated thus :—

$$6FeCl_2 + K_2Cr_2O_7 + 14HCl$$

Ferrous and dichrome and hydrochloric
chloride acid

$$= 3Fe_2Cl_6 + Cr_2Cl_6 + 2KCl + 7H_2O$$

yield ferric and chromic and potassium and water.
chloride chloride chloride

---

* Unless precautions are taken, the ferrous solution soon becomes more or less completely converted into ferric solution having a yellow colour.

This equation shows that 1 gramme of iron requires 0·878 gramme of dichrome to complete the reaction.

To Prepare a Standard Solution for the Estimation of Iron.

Weigh off 17·6 grammes of pure, dry dichrome. This quantity is, in practice, more convenient than the theoretical amount—17·56 grammes.

Transfer to a graduated litre flask.

Dissolve the salt in about 600 c.c. of distilled water, and, when the solution is at 15·5° C., make up to the mark with distilled water at that temperature.

Pour, if necessary through a dry filter, into a Winchester quart bottle.

Measure another litre of water in the graduated flask, and pour or filter it into the Winchester.

Mix the solution thoroughly.

To Standardise the Dichrome Solution.

Collect the following solutions and articles on the working bench :—

The prepared dichrome solution.

A dilute solution of stannous chloride (see p. 416) in a dropper.

A 5 per cent. solution of mercuric chloride.

A freshly-prepared solution of potassium ferri-cyanide. This must not be confounded with

the more common ferrocyanide. About 0·1 gramme may be dissolved in 100 c.c. of water.

A 2 per cent. solution of ammonium thiocyanate (sulphocyanide).

One or two white porcelain slabs about 10 c.m. (or 4 inches) square.

Stirring rods for the ferricyanide and the thiocyanate solutions.

A porcelain basin about 7 inches diameter.

A glass rod about 8 inches long.

A reagent bottle containing pure re-distilled hydrochloric acid.

A wash-bottle containing hot water.

A burette stand, and

A burette, graduated in one-tenths.

Iron wire, pure by preference, or pure, dry ferrous ammonium sulphate or Mohr's salt (see composition on p. 122).

Clean the burette, first with water, and then with standard dichrome solution. Run off, into a sink, the dichrome solution used for cleaning the burette.

Fix the burette in the stand.

Nearly fill the burette with the dichrome solution, and adjust to zero.

Clean the porcelain slab, and wipe it with a piece of clean filter-paper.

Weigh off accurately about 2 grammes of Mohr's salt, note the weight taken, and transfer to the porcelain basin.

Add about 150 c.c. of distilled water, and about 50 c.c. of hot water.

Add about 20 c.c. of pure re-distilled hydrochloric acid.

Stir until the salt is dissolved.

Proceed to titrate by running in standard dichrome solution to oxidise the ferrous iron.

> The point at which the whole of the ferrous iron has become oxidised to ferric iron is ascertained by placing at intervals a number of drops of a very weak solution of potassium ferricyanide (K_3FeCy_6) on a white glazed tile, and bringing from time to time, on the point of the glass stirring rod, a drop of the iron solution which is being titrated into contact with one of the ferricyanide drops. As long as ferrous iron remains in the solution a blue precipitate or a blue colouration will result from the mixing of the drops of these solutions. As the indication is developed outside of the bulk of the solution which is being examined, the term "external indicator" is used.

Note the quantity of dichrome solution required to complete the reaction.

Calculate as in the following example:—

2·0485 grammes of Mohr's salt, which contains 14·26 per cent. of iron, required 14·34 c.c. of the dichrome solution.

Iron in weighed quantity of Mohr's salt

$$= \frac{2\cdot0485}{14\cdot26} = 0\cdot14365 \text{ gramme.}$$

Value of the dichrome solution

$$\frac{0 \cdot 14365}{14 \cdot 34} = 0 \cdot 010024.$$

∴ Every 1 c.c. of the standard dichrome solution = 0·01002 gramme of iron.

Make one or two additional estimations, and if all nearly agree, the mean may be taken. The winchester may then be labelled so as to show the strength of the solution and the date of standardising.

EXERCISES IN THE ESTIMATION OF IRON BY MEANS OF STANDARD DICHROME SOLUTION.

Collect the solutions and articles mentioned on pp. 131 and 132.

Clean the burette, first with water, and then with standard dichrome solution. Run off, into a sink, the dichrome solution used for cleaning the burette.

Fix the burette in the stand.

Nearly fill the burette with the standard solution, and adjust to zero.

Weigh off accurately about 2 grammes of pure, dry Mohr's salt, and note the weight taken.

Transfer the weighed quantity to a 7-inch porcelain basin.

Add about 150 c.c. of distilled water, 50 c.c. of hot water, and 20 c.c. of pure, redistilled hydrochloric acid.

Stir until the salt is dissolved.

Proceed to titrate by running in standard dichrome solution to oxidise the ferrous iron.

The point at which the whole of the ferrous iron has become oxidised to ferric iron is ascertained by placing at intervals a number of drops of a very weak solution of potassium ferricyanide (K_3FeCy_6) on a white glazed tile, and bringing from time to time, on the point of the glass stirring rod, a drop of the iron solution which is being titrated into contact with one of the ferricyanide drops. As long as ferrous iron remains in the solution a blue precipitate or a blue colouration will result from the mixing of the drops of these solutions. As the indication is developed outside of the bulk of the solution which is being examined, the term " external indicator " is used.
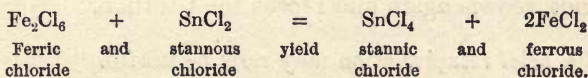
Note the quantity of solution required to complete the reaction.

Calculate as shown in the example on p. 126.

Having, by means of the dichrome solution, oxidised the iron to the ferric state, the iron in the solution should now be reduced to the ferrous condition.

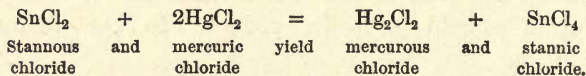**Solutions containing ferric iron are reduced** by the addition of acid solution of stannous chloride ($SnCl_2$), which is cautiously added, especially as the yellow colour of the ferric solution disappears.

The reaction may be set down thus:—

Fe_2Cl_6	+	$SnCl_2$	=	$SnCl_4$	+	$2FeCl_2$
Ferric chloride	and	stannous chloride	yield	stannic chloride	and	ferrous chloride.

To find the exact point at which the reduction to ferrous chloride is completed, a drop of the iron solution should be brought into contact with a drop of ammonium thiocyanate (sulphocyanide) solution on a white glazed slab, or on a piece of drop-reaction paper. Where the drops mix with each other a distinct blood-red colour will be shown if ferric iron is present. As the reduction proceeds it will be found that the colour is less distinct as each successive drop is mixed with a fresh drop of the iron solution. When only a faint pink colour results from the joining of the drops, it may be safely assumed that all the ferric iron has been reduced.

To guard against presence of excess of stannous chloride (which excess would spoil the accuracy of the estimation), about 4 c.c. of a 5 per cent. solution of mercuric chloride is added to the iron solution which has just been reduced. Excess of stannous chloride, if present, forms a white precipitate when the mercuric chloride is added. The following equation represents the change :—

$SnCl_2$	$+$	$2HgCl_2$	$=$	Hg_2Cl_2	$+$	$SnCl_4$
Stannous chloride	and	mercuric chloride	yield	mercurous chloride	and	stannic chloride.

The ferrous solution will then be ready for re-titrating with standard dichrome solution.

Proceed with the titration as before. The result should correspond with the one previously obtained. If not, reduce again and repeat the titration.

A brief recapitulation may now be useful.

Ferric solutions are yellow-coloured; ferrous solutions are colourless.

Ferric solutions yield a blood-red colour when mixed with solution of ammonium thiocyanate (sulphocyanide); ferrous solutions do not.

Ferrous solutions form a blue precipitate or show a blue colour when mixed with potassium ferricyanide solution; ferric solutions do not.

Stannous chloride reduces ferric solutions to ferrous.

Mercuric chloride precipitates and corrects excess of stannous chloride.

Dichrome oxidises ferrous iron in solution to the ferric state, and is unaffected by presence of manganese or other salts usually present in solutions from iron ores, &c.

With a little practice the *rationale* of the method should become clear, and the points at which oxidation and reduction are completed may be determined with accuracy. The experiments should be carefully worked through by the student.

ESTIMATION OF IRON IN ORE BY MEANS OF STANDARD DICHROME SOLUTION.

Before making an assay by titration, the student should practice the exercises set on the previous pages.

Collect the solutions and articles required (see pp. 131 and 132).

Clean the burette, first with water, and then with some of the standard dichrome solution, and fix it on the stand.

Nearly fill the burette with the dichrome solution and adjust to zero.

The ore, having been carefully sampled, and the sample pounded, mixed well, bottled, and labelled, a portion should be withdrawn for assaying. This portion should be finely-pounded in an agate mortar.

Weigh off accurately 1 gramme of the finely-powdered ore.

Transfer it to a 10-oz. conical flask.

Add about 10 c.c. of pure re-distilled hydrochloric acid.

Place a 2-inch funnel in the neck of the flask, and set the whole on a hot plate so as to hasten solution. Solution may be further facilitated by the addition of stannous chloride in re-distilled hydrochloric acid, care being taken to avoid addition of excess.

When all the iron has dissolved, remove the flask, wash the condensed liquid from the funnel and also the contents of the flask into a 7-inch porcelain basin.

Reduce as directed on pp. 135 and 136.

Proceed to titrate as directed on p. 124.

Note the quantity of standard solution taken.

Calculate the percentage.

EXAMPLE OF CALCULATION.

1 gramme of red hematite ore taken for the estimation.

54·6 c.c. of the standard dichrome solution were

required to complete the oxidation of the iron. Each c.c. of the standard dichrome solution was capable of oxidising 0·01002 gramme of iron.

$$\frac{54 \cdot 6 \times 0 \cdot 01002 \times 100}{1} = 54 \cdot 6 \times 1 \cdot 002.$$

$$54 \cdot 6 \times 1 \cdot 002 = 54 \cdot 71.$$

54·71 = percentage of iron in the sample of ore.

$$54 \cdot 71 \times \frac{10}{7} = 78 \cdot 16.$$

78·16 = percentage of ferric oxide (Fe_2O_3) in the sample.

ESTIMATION OF FERROUS AND FERRIC OXIDES IN AN ORE.

Collect the following solutions and articles on the working bench :—

Standardised dichrome solution (see pp. 131 to 134.

A dilute solution of stannous chloride (see p. 416) in a dropper.

A 5 per cent. solution of mercuric chloride.

A freshly-prepared solution of potassium ferri-cyanide. This must not be confounded with the more common ferrocyanide. About 0·1 gramme may be dissolved in 100 c.c. of water.

A 2 per cent. solution of ammonium thiocyanate (sulphocyanide).

One or two white porcelain slabs.

Stirring rods for the ferricyanide and the thio-cyanate solutions.

A porcelain basin about 7 inches diameter.
A glass rod about 8 inches long.
A reagent bottle containing pure, redistilled hydrochloric acid.
A wash-bottle containing hot water.
A burette stand, and
A burette, graduated in one-tenths.

Select two 175 c.c. (about 6 ozs.) conical flasks. Fit one with a tight-fitting one-hole rubber cork, and the other with a two-hole rubber cork, and to these fit a doubly-bent glass tube, all as shown in Fig. 19.
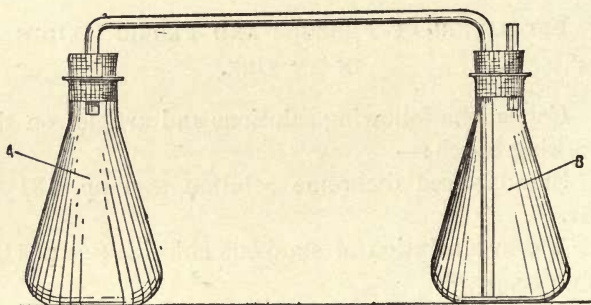

Fig. 19.—Flasks for dissolving iron ore.

Read the general observations on the estimation of iron by means of standard dichrome solution (see p. 131).

For notes on the disintegration of ores, see pp. 251 to 254.

Outline of the Process.—On dissolving ore containing ferrous and ferric oxides in hydrochloric

acid, changes take place which may be represented by the equations—

$$FeO + 2HCl = FeCl_2 + H_2O.$$
$$Fe_2O_3 + 6HCl = Fe_2Cl_6 + 3H_2O.$$
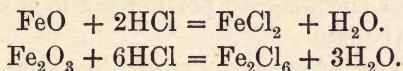
Where, as in this instance, it is intended to estimate ferrous and ferric oxides separately, all apparatus and solutions should be in readiness before beginning to dissolve the ore, so that as soon as the ore is dissolved (as far as practicable), titration may be proceeded with before the solution of the ore appreciably suffers from natural oxidation by exposure to air. Precautions are taken to exclude air while the iron in the ore is being dissolved.

The solution from the weighed portion of the ore is titrated with standard dichrome solution. This effects the conversion of the ferrous compound into ferric. The amount of dichrome solution required is noted and all the ferric and chromic compounds are then reduced by stannous chloride to the ferrous and chromous condition. The solution in the basin is again titrated, and the quantity of standard dichrome solution required for this second titration is a measure of the total amount of iron in the ore. The percentage of ferric iron is esti- mated by difference.

Details of the Process.—Measure about 60 c.c. of boiling distilled water into the conical flask (B, Fig. 19).

Dry the other flask, and put about 1 gramme of sodium carbonate into it.

Weigh off 1 gramme of the finely-powdered sample of the ore.

Transfer the weighed portion to the flask containing the carbonate.

Add 10 c.c. of pure re-distilled hydrochloric acid.

At once close the flask with the cork (which should be moistened) to which the glass tube has been fitted.

Press, with a spiral motion, the cork firmly into the neck of the flask.

Dip the other end of the tube into the hot water in the other flask (see Fig. 17).

Apply heat gently until the iron is dissolved.

Remove the apparatus from the source of heat (hot plate or Bunsen burner), and allow the hot water to suck back into the dissolving flask.

Wash the solution, with hot water, into the basin.

Add about 50 c.c. of hot water.

Run in standard dichrome solution while briskly stirring.

Test from time to time by taking a drop from the basin on the end of the stirring rod and dropping on to a "spot" of potassium ferricyanide solution on the white slab or a piece of drop-reaction paper.

Continue the addition of the standard dichrome solution until, on testing, the desired tint is reached.

The point at which the whole of the ferrous iron has become oxidised to ferric iron is ascertained by placing at intervals a number of drops of a very weak solution of potassium ferricyanide (K_3FeCy_6) on a white glazed tile, and bringing

from time to time, on the point of the glass stirring rod, a drop of the iron solution which is being titrated into contact with one of the ferricyanide drops. As long as ferrous iron remains in the solution a blue precipitate or a blue colouration will result from the mixing of the drops of these solutions. As the indication is developed outside of the bulk of the solution which is being examined, the term " external indicator " is used.

It is essential that this tint should be as near as possible to that at which the operation was stopped when standardising the dichrome.

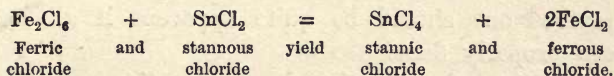Read off and note the volume of dichrome solution which has been run in from the burette.

Withdraw the basin, and refill the burette with standard dichrome solution.

Adjust the solution to zero.

Reduce the solution in the basin by adding solution of stannous chloride (see p. 416) while stirring briskly.

Solutions containing ferric iron are reduced by the addition of acid solution of stannous chloride ($SnCl_2$), which is cautiously added, especially as the yellow colour of the ferric solution disappears.

The reaction may be set down thus :—

Fe_2Cl_6	+	$SnCl_2$	=	$SnCl_4$	+	$2FeCl_2$
Ferric chloride	and	stannous chloride	yield	stannic chloride	and	ferrous chloride.

To find the exact point at which the reduction to

ferrous chloride is completed, a drop of the iron solution should be brought into contact with a drop of ammonium thiocyanate (sulphocyanide) solution on a white glazed slab, or on a piece of drop-reaction paper. Where the drops mix with each other a distinct blood-red colour will be shown if ferric iron is present. As the reduction proceeds it will be found that the colour is less distinct as each successive drop is mixed with a fresh drop of the iron solution. When only a faint pink colour results from the joining of the drops, it may be safely assumed that all the ferric iron has been reduced.

When reduction appears to be nearly completed, test for presence of ferric iron.

If necessary, cautiously drop in more of the stannous chloride solution, stir well, and test again.

Continue to add stannous chloride and to test.

When, on applying the test, only a faint pink colour is developed, add about 4 c.c. of a 5 per cent. solution of mercuric chloride to correct, if necessary, any excess of stannous chloride.

Again test on a thiocyanate spot, and make sure that no ferric iron is present.

Run in from the burette two drops of the standard dichrome solution.

Test on a sulphocyanide spot. The contrast between the colour of this last "spot" and the previous one should be quite apparent if all has been properly done.

Complete the titration by the cautious addition of standard dichrome solution.

Note the quantity of standard solution used to complete the oxidation.

Calculate the result.

EXAMPLE OF CALCULATION.

One gramme of sample of clayband ironstone taken for the estimation.

Each c.c. of the standard dichrome solution was capable of oxidising 0·01001 gramme of iron.

29·93 c.c. of the standard dichrome solution were required to oxidise the ferrous iron, and, after reduction, 31·8 c.c. were required to complete the oxidation of the iron.

Ferrous iron—

$$\frac{29 \cdot 93 \times 0 \cdot 01001 \times 100}{1} = 29 \cdot 93 \times 1 \cdot 001,$$

$$29 \cdot 93 \times 1 \cdot 001 = 29 \cdot 96.$$

29·96 = percentage of ferrous iron.

Total iron—

$$\frac{31 \cdot 8 \times 0 \cdot 0100 \times 100}{1} = 31 \cdot 8 \times 1 \cdot 001,$$

$$31 \cdot 8 \times 1 \cdot 001 = 31 \cdot 83.$$

31·83 = percentage of total iron.

Then, Total iron,   .   .   . = 31·83 per cent.
     Ferrous iron, .   .   . = 29·96 ,,

      Ferric iron, by difference, = 1·87   ,,

10

Ferrous oxide (FeO)—

$$29 \cdot 96 \times \tfrac{9}{7} = 38 \cdot 52,$$

and $38 \cdot 52$ = percentage of ferrous oxide.

Ferric oxide (Fe_2O_3)—

$$1 \cdot 87 \times \tfrac{10}{7} = 2 \cdot 67,$$

and $2 \cdot 67$ = percentage of ferric oxide.

ESTIMATION OF CHROMIUM.

CHROMIUM IN STEEL.—STEAD'S METHOD.

Outline of the Process.—The sample, preferably in moderately-fine drillings or turnings, is dissolved in sulphuric acid and oxidised by permanganate. Hydrochloric acid is added, and the solution is boiled till all chlorine is driven off. To the clear solution, excess of ferrous salt in known quantity is added. The oxidation of ferrous iron due to the chromium in the steel, is ascertained, by difference, on titrating with standard dichrome solution (see pp. 131 to 137 for details of dichrome titrations).

Details of the Process.—Weigh off 2 grammes of the steel drillings or turnings. For steels containing a small percentage of chromium, a larger quantity of sample should be taken.

Transfer the weighed portion to a beaker of about 1,000 c.c. capacity.

Add 30 c.c. of dilute sulphuric acid [1 of acid (sp. gr. 1·84) to 3 of water].

Pour on to the sample in the beaker.

Cover with a clock glass.

Set the beaker on a hot plate and allow to remain until crystals begin to form in the solution.

Wash down any crystals which may have crept up the sides of the beaker.

Add about 70 c.c. of hot water.

Filter, collecting the filtrate in a glazed porcelain basin of about 18 cm. (about 7 inches) diameter.

Dilute with about 200 c.c. of water.

Add a solution of 0·5 gramme of potassium permanganate in a little water.

Boil for ten minutes. At this stage the liquid should still be of a pink colour. If not, add potassium permanganate crystals until it is so.

Mix 40 c.c. of hydrochloric acid (1·16 sp. gr.) with an equal bulk of water, and add to the liquid in the beaker. It is necessary to add dilute acid, and to keep it dilute throughout the process.

Boil, and gently continue the boiling till the brown peroxide dissolves.

Add 150 c.c. of boiling water, and boil till about 100 c.c. of water has evaporated.

The solution should then be free from chlorine. This may be confirmed by holding a piece of litmus paper in the vapour from the basin. The colour will not be discharged if all the chlorine has been driven off.

The iron and chromium should now be in their highest state of oxidation.

Get ready the following for titration :—

Standard dichrome solution (see pp. 131 to 134).

A burette graduated in one-tenths.

A burette stand.

A glass stirring rod about 20 cm. (or 8 inches) long.

A white glazed porcelain slab about 10 cm. (or 4 inches) square, or a piece of "drop reaction" filter-paper.

A glass or porcelain dish with a freshly-prepared
 solution of potassium ferricyanide. About
 0·1 gramme may be dissolved in 100 c.c. of
 water.

A glass stirring rod, about 10 cm. (or about 4
 inches) long, for the ferricyanide solution.

Clean the burette.

Fill the burette with standard dichrome solution,
and run off the solution into a sink.

Again fill the burette with standard dichrome
solution.

Fix the burette in the stand.

Clean the porcelain slab, and wipe it with a piece
of clean filter-paper.

Weigh off about 4 grammes of Mohr's salt (see p.
122), and note the weight taken.

Put the weighed portion in the basin, and stir
until the salt is dissolved.

Adjust the solution in the burette to zero.

Place the basin under the burette.

From the burette run in dichrome solution to
oxidise the ferrous iron.

The point at which the whole of the ferrous
iron has become oxidised to ferric iron is ascer-
tained by placing at intervals a number of drops
of a very weak solution of potassium ferricyanide
(K_3FeCy_6) on a white glazed tile, and bringing
from time to time, on the point of the glass
stirring rod, a drop of the iron solution which
is being titrated into contact with one of the

ferricyanide drops. As long as ferrous iron remains in the solution a blue precipitate or a blue colouration will result from the mixing of the drops of these solutions. As the indication is developed outside of the bulk of the solution which is being examined, the term "external indicator" is used.

Note the quantity of solution required to complete the reaction.

Calculate as in the following example:—

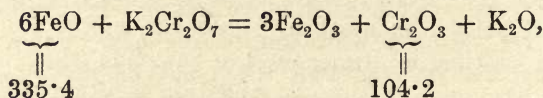Sample of steel taken . . = 2·000 grammes.

    ,,   Mohr's salt taken . = 4·007   ,,

Iron in Mohr's salt $\dfrac{4 \cdot 007 \times 14 \cdot 26}{100} = 0 \cdot 5714$ gramme.

Dichrome solution required = 23·10 c.c., of which each c.c. = 0·01013 gramme of iron.

$$23 \cdot 1 \times 0 \cdot 01013 = 0 \cdot 234.$$

Grammes.

Iron in Mohr's salt . . . . . = 0·5714

  ,, represented by the standard dichrome

      used . . . . . . = 0·2340

  ,, oxidised per chromium in the example = 0·3374

Equation—

$$6\underbrace{FeO}_{335\cdot4} + K_2Cr_2O_7 = 3Fe_2O_3 + \underbrace{Cr_2O_3}_{104\cdot2} + K_2O,$$

which shows that in this reaction 335·4 parts, by

weight, of iron are equivalent to 104·2 parts, by weight, of chromium. Then

$$\frac{104\cdot2 \times 100}{335\cdot4} = 31\cdot067.$$

31·067 = Factor.

$$\text{Log } 31\cdot067 = 1\cdot4922993.$$

The percentage of chromium is found by multiplying the "iron oxidised" by this factor and dividing by the amount of sample taken.

In this instance,

$$\frac{0\cdot3374}{2} \times 31\cdot067 = 5\cdot24.$$

5·24 = percentage of chromium in the sample of steel.

Estimation of Chromium in Ferro-chrome.— Saniter's Method.

Outline of the Process. — The sample for analysis should be finely pounded and mixed well. A portion should then be taken and pulverised in an agate mortar, so that the whole of it will pass through a sieve of 10,000 holes per square inch = 100 wires each way per square inch. The weighed sample is fused at a moderate temperature in a mixture of sodium and barium peroxides. A soluble "melt," containing the chromium, iron, &c., of the sample in their highest state of oxidation, is thus obtained.

This is dissolved, and when all the materials for a dichrome titration are ready, a weighed quantity of a substance containing a known amount of ferrous iron —which must be in excess—is also dissolved, and the solution is titrated with standard dichrome solution. The oxidation of the ferrous iron, due to the chromium in the ferro-chrome, is thus ascertained by difference.

Details of the Process.—Weigh off about 4 grammes of sodium peroxide, and about 0·75 gramme of barium peroxide.

Mix the weighed portions, and transfer to a nickel capsule of 7·5 cm. (about 3 inches) diameter.

Weigh off accurately about 0·3 to 0·5 gramme of the pulverised sample, and note the weight taken.

Add to the peroxides in the nickel capsule, and mix all well.

Hold the capsule by means of crucible tongs, or on a pipe-clay support fastened to a convenient handle, in the flame of a good Bunsen burner until the mass begins to melt. The temperature should be just short of visible red. Then impart a circular motion to the capsule while keeping it in the flame and taking care not to allow the solids to settle to the bottom. Fusion may be effected in a muffle at a dull red heat.

Continue the fusing for about three minutes. This should yield a very liquid melt.

Allow the capsule and contents to cool.

Place in a glazed porcelain basin of 18 cm. (about 7 inches) diameter.

Pour water into the nickel capsule, and allow the melt to dissolve.

Pour the solution into the porcelain basin.

Rinse the remainder from the nickel capsule, using a rubber end to detach any portion which sticks. By boiling a little water in the nickel capsule any still-clinging melt may be loosened.

Add about 300 c.c. of hot water to the contents of the porcelain basin.

Add about 0·3 gramme of potassium permanganate crystals. The quantity added should produce a strong pink colour, which does not disappear until gently boiled for more than ten minutes after the addition of the dilute hydrochloric acid noted below.

Mix 40 c.c. of hydrochloric acid (1·16 sp. gr.) with an equal bulk of water, and add to the liquid in the basin. It is necessary to add dilute acid, and to keep it dilute throughout the process.

Boil till clear.

Add 150 c.c. of hot water.

Boil for ten minutes to make sure that all chlorine has been driven off. This may be confirmed by holding a piece of litmus paper in the vapour from the basin. The colour will not be discharged if all the chlorine has been driven off.

The iron and chromium should now be in their highest state of oxidation.

Get ready the following for titration :—

> Standard dichrome solution (see pp. 131 to 134).
>
> A burette graduated in one-tenths.
>
> A burette stand.
>
> A glass stirring rod about 20 cm. (or 8 inches) long.
>
> A white glazed porcelain slab about 10 cm. (or 4 inches) square, or a piece of "drop reaction" filter-paper.
>
> A glass or a porcelain dish with a freshly-prepared solution of potassium ferricyanide. About 0·1 gramme may be dissolved in 100 c.c. of water.
>
> A glass stirring rod, about 10 cm. (or about 4 inches) long, for the ferricyanide solution.

Clean the burette.

Fill the burette with standard dichrome solution, and run off the solution into a sink.

Again fill the burette with standard dichrome solution.

Fix the burette in the stand.

Clean the porcelain slab, and wipe it with a piece of clean filter-paper.

Place on the slab at intervals a series of drops of the ferricyanide solution.

Weigh off about 5·5 grammes of Mohr's salt (see p. 122), and note the weight taken.

Put the weighed portion in the basin, and stir until the salt is dissolved.

Adjust the solution in the burette to zero.

Place the basin under the burette.

From the burette run in dichrome solution to oxidise the ferrous iron.

The point at which the whole of the ferrous iron has become oxidised to ferric iron is ascertained by placing at intervals a number of drops of a very weak solution of potassium ferricyanide (K_3FeCy_6) on a white glazed tile, and bringing from time to time, on the point of the glass stirring rod, a drop of the iron solution which is being titrated into contact with one of the ferricyanide drops. As long as ferrous iron remains in the solution a blue precipitate or a blue colouration will result from the mingling of the drops of these solutions. As the indication is developed outside of the bulk of the solution which is being examined, the term "external indicator" is used.

Note the quantity of solution required to complete the reaction.

Calculate as in the following example :—

EXAMPLE OF CALCULATION.—

Sample of ore taken .   .   .   = 0·435   gramme.
    „   Mohr's salt taken   .   = 4·7405 grammes.
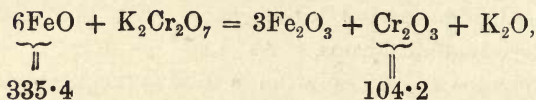Iron in Mohr's salt taken

$$= \frac{4·7405 \times 14·26}{100} = 0·676 \quad \text{gramme.}$$

Dichrome solution required = 11·18 c.c., of which each c.c. = 0·0102 gramme of iron.

$$11·18 \times 0·0102 = 0·1140.$$

Iron in Mohr's salt   .   .   .   = 0·676 gramme.
  „   represented by the standard
      dichrome used, .   .   .   = 0·114   „
  „   oxidised by chromium in the   ———
      sample   .   .   .   .   = 0·562   „

Equation—

$$6FeO + K_2Cr_2O_7 = 3Fe_2O_3 + \underbrace{Cr_2O_3}_{} + K_2O,$$

$$\underbrace{}_{335·4} \qquad \qquad 104·2$$

which shows that in this reaction 335·4 parts, by weight, of iron are equivalent to 104·2 parts, by weight, of chromium. Then

$$\frac{0·562 \times 104·2 \times 100}{335·4 \times 0·435} = \frac{0·562}{0·435} \times 31·067 = 40·139.$$

40·14 ≑ percentage of chromium in the sample of ferro-chrome.

ESTIMATION OF CHROMIC OXIDE IN CHROME IRON ORE.

SANITER'S METHOD.

Outline of the Process. — The finely-ground, weighed sample is heated along with sodium peroxide in a nickel capsule. The "melt" is dissolved, acidified with hydrochloric acid, and peroxidised by permanganate. Chlorine is driven off by boiling. All the oxidisable components of the ore are then in their highest state of oxidation. A known quantity—which must be in excess—of ferrous salt is dissolved in the solution and is acted on by the chromate from the ore, which converts an equivalent amount of ferrous oxide to the ferric state, thus :—

$$Na_2Cr_2O_7 + 6FeO = 3Fe_2O_3 + Cr_2O_3 + Na_2O,$$
$$\text{or } 2CrO_3 + 6FeO = Cr_2O_3 + 3Fe_2O_3.$$
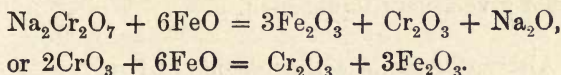
The amount of ferrous oxide unacted on is determined by titrating with standard dichrome solution as in the estimation of iron (but without further addition of ferrous salt), as directed on pp. 134 and 135 for details of bichrome titrations.

Details of the Process.—The first stage is the fusing of the finely-ground sample so as to obtain a good melt. For this purpose two good methods are available.

(A) Weigh off about 3 grammes of sodium peroxide. Transfer the weighed portion to a nickel capsule of about 7·5 cm. (3 inches) diameter.

Weigh off accurately about 0·5 gramme of the finely-ground sample—the sample should be ground

as fine as possible in an agate mortar—and note the amount taken.

Add the weighed portion to the sodium peroxide in the capsule, and mix thoroughly.

Hold the capsule, by means of crucible tongs or on a pipeclay support fastened to a convenient handle, in the flame of a good Bunsen burner until the mass begins to melt. The temperature should be just short of visible red. Then impart a circular motion to the basin while keeping it in the flame, and taking care not to allow the ore to settle to the bottom. Fusion may be effected in a muffle furnace at a dull red heat.

Continue the fusing for about three minutes. This should give a very liquid melt.

Alternatively the following method of fusing may be followed :—

(B) Messrs. James H. Walton, Junr., and Herman A. Scholz give, in the *American Chemical Journal,* xxxix., No. 7,[*] details of a method for the rapid decomposition of chrome iron ore. The mixture prescribed by them is—

> 0·5 gramme chrome iron ore (through 200 mesh seive).
> 8·0 grammes sodium peroxide.
> 0·3 gramme potassium persulphate.
> 2·0 grammes iron pyrites.
> 0·3 gramme magnesium powder.

The correct proportions appear to depend on the

[*] See *Chemical News,* 14th August, 1908.

richness of the pyrites. With rich pyrites the reaction is violent. But it is not difficult to adjust the proportions.

The mixture is placed in a nickel capsule and ignited by means of a thin piece of magnesium wire. Very little damage is done to the capsule, and a nice liquid melt is easily obtained.

Whichever method may have been adopted—either A or B:

Allow the capsule and contents to cool.

Place in a glazed porcelain basin of about 18 cm. (about 7 inches) diameter.

Pour water into the nickel capsule and allow the melt to dissolve.

Pour the solution into the porcelain basin.

Rinse the remainder from the nickel capsule, using a rubber end to detach any portion which sticks. By boiling a little water in the capsule, any still-clinging melt may be loosened.

Add about 230 c.c. of hot water to the contents of the porcelain basin.

Add also 50 c.c. of water in which a few crystals of potassium permanganate have been dissolved.

The theoretical amount of permanganate required to oxidise 1 gramme of FeO to Fe_2O_3 is 0·44 gramme.

Enough permanganate should be added to impart to the liquid a decided pink colour which does not disappear until gently boiled for more than ten minutes after the addition of the dilute hydrochloric acid noted below.

Mix 40 c.c. of hydrochloric acid (1·16 sp. gr.) with an equal bulk of water, and add to the liquid in the

basin. It is necessary to add dilute acid, and to keep it dilute throughout the process.

Boil till clear.

Add 150 c.c. of hot water.

Boil for ten minutes, to make sure that all chlorine has been driven off. This may be confirmed by holding a piece of litmus paper in the vapour from the beaker. The colour will not be discharged if all the chlorine has been driven off.

The iron and chromium should now be in their highest state of oxidation.

Get ready the following for titration :—

Standard dichrome solution (see pp. 131 to 134).

A burette graduated in one-tenths.

A burette stand.

A glass stirring rod about 20 cm. (or 8 inches) long.

A white glazed porcelain slab about 10 cm. (or 4 inches) square, or a piece of " drop reaction " filter-paper.

A glass or porcelain dish with a freshly-prepared solution of potassium ferricyanide. About 0·1 gramme may be dissolved in 100 c.c. of water.

A glass stirring rod, about 10 cm. (or about 4 inches) long, for the ferricyanide solution.

Clean the burette.

Fill the burette with standard dichrome solution, and run off the solution into a sink.

Again fill the burette with standard dichrome solution.

Fix the burette in the stand.

Clean the porcelain slab, and wipe it with a piece of clean filter-paper.

Place on the slab at intervals a series of drops of the ferricyanide solution.

Weigh off about 4·5 grammes of Mohr's salt (see p. 122), and note the weight taken.

Put the weighed portion in the basin, and stir until the salt is dissolved.

Adjust the solution in the burette to zero.

Place the basin under the burette.

From the burette run in dichrome solution to oxidise the ferrous iron.

The point at which the whole of the ferrous iron has become oxidised to ferric iron is ascertained by placing at intervals a number of drops of a very weak solution of potassium ferricyanide (K_3FeCy_6) on a white glazed tile, and bringing from time to time, on the point of the glass stirring rod, a drop of the iron solution which is being titrated into contact with one of the ferricyanide drops. As long as ferrous iron remains in the solution a blue precipitate or a blue colouration will result from the mingling of the drops of these solutions. As the indication is developed outside of the bulk of the solution which is being examined, the term "external indicator" is used.

Note the quantity of solution required to complete the reaction.

11

Calculate as in the following example :—

EXAMPLE OF CALCULATION.—

Weight of ore taken . . = 0·5031 gramme.
    ,,   Mohr's salt taken = 5·1166 grammes.

Iron in Mohr's salt taken

$$= \frac{5 \cdot 1166 \times 14 \cdot 26}{100} = 0 \cdot 72963$$

Dichrome solution required = 22·6 c.c., of which each c.c. = 0·0102 gramme of iron.

$$22 \cdot 6 \times 0 \cdot 0102 = 0 \cdot 23052.$$

Iron in Mohr's salt . . . = 0·72963 gramme.
  ,, represented by the standard
        dichrome used, . . = 0·23052   ,,
  ,, oxidised by Cr_2O_3 in the
        sample of ore . . = 0·49911   ,,

Equation—

$$6FeO + K_2Cr_2O_7 = 3Fe_2O_3 + \underbrace{Cr_2O_3}_{152 \cdot 2} + K_2O,$$
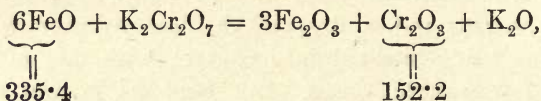
$$\underbrace{}_{335 \cdot 4}$$

which shows that, in this reaction, 335·4 parts. by weight, of iron are equivalent to 152·2 parts, by weight, of chromic oxide. Then—

$$\frac{0 \cdot 4991 \times 152 \cdot 2 \times 100}{335 \cdot 4 \times 0 \cdot 5031} = \frac{0 \cdot 4991}{0 \cdot 5031} \times 45 \cdot 38 = 45 \cdot 02.$$

45·02 = percentage of Cr_2O_3 in the sample of ore.

ESTIMATION OF NICKEL.

NICKEL IN STEEL—GRAVIMETRIC METHOD.

SEPARATING AS SULPHIDE, AND WEIGHING THE ROASTED RESIDUE.

Outline of the Process.—The weighed sample of the steel is dissolved, and the excess acid is carefully neutralised. A large quantity of water and a measured amount of ammonium acetate solution are added. On boiling, a bulky precipitate consisting of basic hydrate and acetate of iron is formed, and the solution containing the nickel is separated on filtering and washing. The solution is concentrated by evaporation. This second precipitate is dissolved in acid, the solution is neutralised, and the iron is reprecipitated, drained into a filter, and washed. The second filtrate and washings are also concentrated, and, if necessary, the two concentrates are filtered, all the liquid being collected in a large flask, and ammonia added. Sulphuretted hydrogen is then passed into the liquid. This causes the formation of nickel sulphide—

$$NiCl_2 + H_2S = NiS + 2HCl.$$
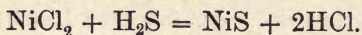
The precipitate is collected on a filter, washed dried, and roasted till all the nickel sulphide is converted into oxide—

$$2NiS + 3O_2 = 2NiO + 2SO_2.$$
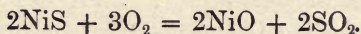
The percentage of nickel is calculated from the weight of the nickel oxide.

Details of the Process.—Weigh off 2·5 grammes of the sample. Transfer the weighed portion to a 1,200 c.c. (about 40-oz.) globular Bohemian flask.

Add 35 c.c. of 1·42 specific gravity nitric acid along with 15 c.c. of water.

Set the flask on a hot plate to hasten solution.

When the sample has dissolved add about 15 c.c. of hot water.

Boil.

Add ammonia liquor till a slight permanent precipitate forms and remains in the hot liquid even after vigorous shaking. Much of the success of the estimation depends on the accuracy with which the neutralisation is effected.

Add about 400 c.c. of cold water.

Add 45 c.c. of ammonium acetate solution (see p. 401).

Boil briskly over the flame of a 16 mm. (about ⅝-inch) Bunsen burner. If the Bohemian flask is set on a tripod, the top of which is of stout iron wire, the contents may be boiled over a large Bunsen flame, no gauze being required. When the top of the tripod has sharp edges such procedure is risky.

> Prepare a 28 cm. (about 10-inch) folded filter of No. 598 C. S. and S. or other thick filter-paper, place it in an 18 cm. (about 7-inch) funnel, saturate it with hot water, and place it in a large filter stand (see Fig. 7, p. 36). Set under it a Berlin basin 7 inches diameter, or larger.

Allow the *boiling* to continue for about half a minute. If the liquid nearly froths over, remove the flask till the brisk action ceases; replace on the tripod, and allow the rapid boiling to continue. It may be necessary to remove and replace two or three times. A voluminous brown or chocolate-coloured precipitate should be formed, from which a clear colourless liquid should drain away quickly when on the filter.

Immediately the boiling has finished, pour the contents of the flask on to the prepared filter, taking care not to rest the neck of the hot flask on the edge of the glass funnel, or the former may crack.

Rinse the flask twice with hot water and pour the rinsings on to the filter. Allow the liquid to drain off thoroughly into the basin.

Wash twice with hot water, collecting the washings in the basin.

Set the basin containing the filtrate and washings over a Bunsen burner, or on a hot plate, so as to evaporate the liquid to small bulk.

Place the flask in which solution of the weighed sample had been effected under the stem of the funnel.

Dissolve the iron precipitate on the filter by means of hot hydrochloric acid and water, collecting all the solution and washings in the flask.

Neutralise with ammonia liquor as before.

Add 45 c.c. of ammonium acetate solution (see p. 401).

Boil, filter, and wash as before, collecting the filtrate and washings in a Berlin basin of 18 cm. (about 7 inches) diameter.

Evaporate the solution to small bulk, and add it to the solution which has been evaporating in the other basin.

If necessary, filter and wash.

Collect the concentrated solutions in a large conical flask, add about 10 c.c. of ordinary pure acetic acid, and pass a rapid stream of sulphuretted hydrogen through the liquid until a precipitate ceases to form and the solution smells strongly of the gas.

Boil off the excess of sulphuretted hydrogen.

Filter through a 12·5 cm. Swedish filter and wash thoroughly with hot water.

The washed residue may be dissolved in hydrochloric acid and again treated with sulphuretted hydrogen to cause the reprecipitation of nickel sulphide, which should be collected on a filter and washed as before. Or the nickel in the solution may be precipitated by sodium hydrate, the precipitate collected, washed, dried, ignited, and weighed as nickel oxide.

The filtrate and washings may be used for the estimation of manganese.

Place the funnel containing the filter-paper and precipitate on a dryer on a hot plate (see Fig. 4, p. 14), and allow to remain till dried.

Ignite the dried paper and precipitate in a tared platinum or porcelain crucible in a muffle furnace which is at a red heat. Allow to remain in the hot muffle till the roasting is completed—45 minutes at least.

Allow to cool in a desiccator, weigh, and note the weight.

Repeat the roasting for about 30 minutes.
Allow to cool in a desiccator and reweigh.
Calculate the result.

Pure nickel oxide contains 78·581 per cent. of nickel, and when 2·5 grammes are taken for the estimation the factor for finding the percentage is—

$$\frac{78 \cdot 581}{2 \cdot 5} = 31 \cdot 432.$$

Log 31·432 = 1·4973720.

EXAMPLE OF CALCULATION—

Weight of precipitate + crucible

	+ ash . . . = 18·9031 grammes.
„	crucible . . . = 18·8264 „
„	precipitate + ash . = 0·0767 gramme.
„	ash . . . . = 0·0008 „
„	precipitate . . = 0·0759 „

$$0 \cdot 0759 \times 31 \cdot 432 = 2 \cdot 386.$$

2·39 ≑ percentage of nickel in the sample of steel.

Estimation of Nickel in Steel.
Gravimetric Dimethylglyoxime Method.

Outline of the Process.—This excellent method by O. Brunck (see *Zeit. f. angewandte Chemie*, 1907, vol. ii.) is based on the fact that when an alcoholic solution of dimethylglyoxime is added to a neutral or slightly alkaline solution containing nickel, a voluminous scarlet-red precipitate containing all the nickel is formed. This is collected on a filter, and is easily washed. The precipitate is then washed into a tared basin, dried on a water bath, and weighed. From the weight of the pure dried precipitate the percentage of nickel present is calculated.

Details of the Process.—Weigh off 1 gramme of the drillings from the sample.

Transfer to an 800 c.c. Bohemian or Jena beaker.

Dissolve in the smallest workable quantity of 1·16 specific gravity hydrochloric acid—20 c.c. is usually sufficient — and boil, with further small additions of hydrochloric acid, to make sure of the iron being in the ferric state.

Filter if necessary, collecting the filtrate (and washings) in a 500 c.c. beaker. Dilute to about 350 c.c.

Wash well with warm water.

Add about 1 gramme of pure **tartaric acid** either in crystals or in solution.

Heat the solution to about 50° C.

Add enough dimethylglyoxime solution (see p. 405) to precipitate all the nickel present. Good

results were obtained on working with the following quantities :—

Steel containing about						
Steel containing about		0·5	per cent. of nickel,		15	c.c.
„	„	1·0	„	„	20	„
„	„	1·5	„	„	30	„
„	„	2·0	„	„	40	„
„	„	2·5	„	„	45	„
„	„	3·0	„	„	50	„
„	„	3·5	„	„	55	„

Add ammonia liquor until the solution is faintly alkaline—excess must be avoided—and stir the solution well. This will cause a precipitation of a scarlet-red precipitate, which is a little difficult to see at first in the deep coloured solution. Dimethylglyoxime precipitates nickel only; mixed impurities are easily separated by washing.

Collect the filtrate on a 15 cm. smooth filter-paper.

Wash the precipitate thoroughly with warm water.

Open out the filter-paper, and, with a fine-spout wash bottle containing warm water, wash the precipitate into a 7·5 cm. (about 3 inches) diameter tared porcelain basin.

Evaporate on the water bath (Fig. 6, p. 21) till the precipitate is completely dried.

Wipe the outside of the basin with a clean cloth which does not leave fluff.

Allow the basin and precipitate to cool in a desiccator.

Weigh, and calculate the result.

The precipitate, when thoroughly washed and

dried on a water bath, consists of $C_8H_{14}N_4O_4Ni$, and contains 20·332 per cent. of nickel.

$$\text{Log } 20·332 = 1·3081801.$$

EXAMPLE—

Weight of basin + precipitate		= 23·4463 grammes.
„ basin	. .	= 23·3180 „
„ precipitate	.	= 0·1283 gramme.

$$0·1283 \times 20·332 = 2·61.$$

$2·61 =$ percentage of nickel in the sample of steel.

ESTIMATION OF NICKEL IN STEEL BY ELECTRIC CURRENT.

Weigh off about 0·3 gramme of the steel—which should be in the form of fine turnings or drillings—and note the weight taken.

Transfer the weighed sample to a beaker $11·5 \times 7·5$ cm. ($4\frac{1}{2}$ inches deep $\times$ 3 inches) diameter.

Dissolve in minimum excess of nitric acid.

Cautiously add strong sulphuric acid, and evaporate till plentiful fumes appear and crystals form in abundance in the solution.

Cautiously add about 100 c.c. of hot water.

Add ammonia liquor till all the iron is precipitated, then add a slight excess.

Digest for 15 minutes or more on a hot plate.

Connect the positive pole of a battery or accumu-

lator to a platinum spiral, and the negative pole to a weighed platinum gauze cone. Rotating cones, &c., are preferred to stationary ones.

Immerse the couple in the beaker containing the solution.

Allow the electric current to pass through for three hours or more, beginning with 1 ampere and increasing, at intervals of half-an-hour, up to 2 amperes, allowing full strength for the last half hour or more.

Maintain about 4 volts all the time.

Withdraw the beaker containing the solution.

Wash, with water, the cone, &c.

Disconnect.

Wash the cone, firstly with distilled water and then with alcohol.

Dry the cone.

Weigh, and note the weight.

The solution in the beaker may be tested for nickel by transferring, by means of a pipette, some of the clear solution to a test tube and adding sulphuretted hydrogen.

Dissolve the nickel from off the weighed cone and test with solution of sulphocyanide, estimating the iron, if present, by comparing with the colour of a measured solution of known percentage of iron, contained in a corresponding cylinder, to which solution of sulphocyanide, in sufficient quantity, has been added.

The standard solution of iron, for colour comparison, is made by dissolving 0·007 gramme of iron wire in hydrochloric acid and making up to 1 litre

with water. Every 10 c.c. will, therefore, contain nearly 0·00007 gramme of iron = 0·0001 gramme of Fe_2O_3.

The necessary correction for co-precipitated iron is made as directed on pp.   and   .

EXAMPLE—

	Grammes.
Weight of cone + "metal" deposited, . .	15·5211
Weight of cone before the action of the current, ...	15·5125
	0·0086
Deduct weight of Fe_2O_3, . .	0·0003
Weight of nickel, . .	0·0083

Then as 0·31 gramme had been taken,

$$\frac{0·0083 \times 100}{0·31} = 2·677.$$

2·68 ≑ percentage of nickel in the sample of steel.

VOLUMETRIC ESTIMATION OF NICKEL IN NICKEL STEEL.

Outline of the Process.—A weighed portion of the sample is dissolved in acid, and the solution is cooled. Potassium cyanide is added to keep the nickel in solution when the iron is precipitated on being poured into ammonia liquor. The precipitate is separated, and a definite quantity of the clear solution is withdrawn and treated with acid to decompose the cyanide. The solution is then made slightly alkaline, and a cloud of silver iodide is precipitated to act as an indicator. Standard solution of cyanide is now measured from a burette. The first effect is the formation of double cyanide of nickel and potash—a reaction represented by the equation—

$$Ni(NO_3)_2 + 4KCN = Ni(CN)_2 . 2KCN + 2KNO_3.$$
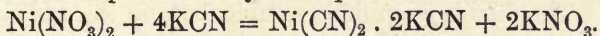
The double cyanide and the potassium nitrate both remain in solution.

When the nickel present has been satisfied, the next drop of cyanide dissolves the cloud of silver iodide, thus indicating the end of the reaction.

The strength of the standard solution being known, it is easy to calculate, from the number of c.c. used, the quantity of nickel present.

Solutions required.

Silver nitrate,   0·5 gramme in 1 litre of water.
Potassium iodide,   20 grammes in 1   „
Potassium cyanide, 50   „   1   „
and **Standard potassium cyanide**, containing 4·44 grammes of pure KCN per litre.

The equation on p. 173 shows that 58·7 parts by weight of Ni require 260·4 parts by weight of KCN.

$$\frac{260\cdot4}{58\cdot7} = 4\cdot44.$$

To prepare the standard potassium cyanide solution, it is necessary in the first place to find the percentage of KCN in the "pure potassium cyanide" supplied or in stock. This is ascertained by dissolving a weighed quantity of the cyanide, and titrating with $\frac{N}{10}$ silver nitrate solution (16·99 grammes of pure silver nitrate dissolved in 1 litre of water).

When silver nitrate solution is added to potassium cyanide solution a double cyanide is formed—

$$AgNO_3 + 2KCN = AgCN \cdot KCN + KNO_3.$$
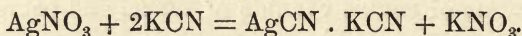
The double cyanide is soluble, but, on the addition of one drop of silver nitrate in excess, a white permanent precipitate or cloud is formed.

1 c.c. of $\frac{N}{10}$ silver nitrate solution = 0·013049 gramme of KCN.

EXAMPLE.—Weighed off 1·0066 gramme of "pure" potassium cyanide, dissolved, and made up to 250 c.c. Mixed well.

Measured off 50 c.c. for titration.

This required 15·20 c.c. of $\frac{N}{10}$ silver nitrate solution. This was confirmed by a duplicate determination.

Then $15\cdot20 \times 0\cdot013049 \times \dfrac{250}{50} \times \dfrac{100}{1\cdot0066} = 98\cdot52.$

98·52 = percentage of KCN in the cyanide.

Then for 1 litre containing 4·44 grammes of KCN,

$$\frac{4 \cdot 44 \times 100}{98 \cdot 52} = 4 \cdot 5067$$

grammes of the "pure" cyanide will be required.

The standard solution of potassium cyanide was prepared accordingly, and, on titration with $\frac{N}{10}$ silver nitrate solution, was found to be correct, each c.c. of the standard solution containing 0·00444 gramme of KCN, which is equivalent to 0·001 gramme of nickel.

Standardising the Cyanide Solution.

0·3315 gramme of pure nickel wire was dissolved, the solution was cooled, diluted to 250 c.c., and 25 c.c. withdrawn for titration. 5 c.c. of the standard silver nitrate and 5 c.c. of the standard potassium iodide solutions were added, and the quantity of standard cyanide solution needed to clear the cloud was delivered from a burette.

The standard cyanide required was 32·5 c.c.

Weight of nickel in the portion of solution used for titration = 0·03315 gramme.

$$\frac{0 \cdot 03315}{32 \cdot 5} = 0 \cdot 00102,$$

and 0·00102 = weight of nickel equal to each c.c. of the standard cyanide solution. This was confirmed by another estimation.

Copper—which is more readily obtained in a state of purity than nickel—may be used for standardising the cyanide solution.

EXAMPLE—

Weight of pure copper taken = 0·3151 gramme.
Copper in $\frac{1}{10}$ withdrawn   . = 0·03151   „

Standard cyanide solution
required   .   .   .   . = 30·3 c.c.

$$\frac{0·03151}{30·3} = 0·00104.$$

Atomic weight of nickel = 58·7
    „   „   copper = 63·6 $= 0·923.$

$$0·00104 \times 0·923 = 0·0009599.$$

0·00096 = weight of nickel equal to each c.c. of the standard solution.

The cyanide solution for titrating may be standardised with steel containing a known percentage of nickel.

Details of the Process.—Weigh off a quantity of the sample, and note the weight taken. For steels containing under 1 per cent. of nickel use 2 grammes of sample; for richer samples use 1 gramme.

Transfer the weighed sample to a 400 c.c. beaker.

For 1 gramme add 25 c.c. of nitric acid of 1·2 specific gravity. [If the steel contains 0·7 per cent. or more of carbon, hydrochloric acid should be used as a solvent.]

Heat until the steel has dissolved and the evolution of nitrous fumes ceases.

When cool, add about 8 c.c. of a 5 per cent solution of potassium cyanide to keep the nickel in solution.

Wash the contents of the beaker into a 250 c.c. flask containing about 50 c.c. of ammonia liquor (sp. gr. 0·88) in 100 c.c. of water.

Make up to the mark with cold water.

Mix well.

Allow the precipitate of ferric hydrate to settle.

Filter about 100 c.c. through a dry filter into a spouted beaker.

Fill a clean 50 c.c. burette with the filtered solution, and run the liquid away.

Fill the burette to zero with more of the filtered solution.

Measure off 50 c.c. into a 350 c.c. (about 12-oz.) conical flask.

Add 15 c.c. of 1·42 specific gravity nitric acid.

Boil briskly for five minutes to destroy the double cyanide.

Neutralise with ammonia liquor and add 1 c.c. in excess.

Dilute to about 100 c.c. with cold water.

Add 5 c.c. of the silver nitrate solution and 2 c.c. of the potassium iodide solution. This causes a cloud of silver iodide, which acts as an indicator.

Fill a 30 c.c. burette with the standard cyanide solution and run the liquid away. This is done to clear the cleaning water out of the burette.

Fill the burette to zero with the standard cyanide solution.

Run standard cyanide solution from the burette into the 12-oz. conical flask—very cautiously and with occasional shaking of the flask towards the end—until the liquid becomes clear.

12

Note the quantity taken, allow for blank, and calculate the result.

EXAMPLE—

Sample weighed off.   . = 1 gramme.
⅕ taken for titration   . = 0·2 „
Standard cyanide solution
    required   .   .   . = 6·04 c.c.

$$\frac{6 \cdot 04 \times 0 \cdot 00102 \times 100}{0 \cdot 2} = 3 \cdot 08.$$

3·08 = percentage of nickel in the sample

Rapid Volumetric Method for the Estimation of Nickel in Steel.

With practice, good results may be obtained by this method. It is, therefore, useful for the estimation of nickel in furnace samples.

Outline of the Process.—A weighed portion of the sample is dissolved and neutralised. A measured amount of standard solution is added, and the iron is precipitated. On filtering and washing, the nickel is separated and is estimated by titrating with standard silver nitrate solution.

The reaction requires 2 equivalents of silver nitrate for each equivalent of nickel.

$$2AgNO_3 = 339 \cdot 8$$
$$Ni = 58 \cdot 7$$
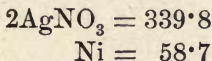
The solutions required for this method are—

Standard silver nitrate solution containing

$$\frac{339 \cdot 8}{58 \cdot 7} = 5 \cdot 789 \text{ grammes in 1 litre of water.}$$

Standard potassium cyanide solution made up so that 1 c.c. equals 1 c.c. of the standard silver nitrate solution. For this purpose the standard cyanide solution should contain 4·44 grammes of KCN per litre.

This is prepared by first ascertaining, by titration with $\frac{N}{10}$ silver nitrate solution, the amount of KCN in

the cyanide by the method described on pp. 174 to 175, and then weighing off and dissolving the required amount of the " pure " cyanide. For example of calculation, see p. 175.

Details of the Process.—Weigh off 1 gramme of the sample.

Transfer the weighed portion to an 800 c.c. beaker.

Add 10 c.c. of 1·2 specific gravity nitric acid, along with 1 c.c. of 1·16 specific gravity hydrochloric acid, and 5 c.c. of water.

Set on a hot plate to dissolve.

When dissolved, wash the solution into a 500 c.c. graduated flask.

Add about 150 c.c. of cold water.

Add dilute ammonia solution (1 of 0·880 specific gravity ammonia in 5 of water) cautiously, and with frequent vigorous shaking, until a slight permanent precipitate forms.

Measure from a burette 10 c.c. of the standard cyanide solution for every 1 per cent. of nickel expected. Measure also 10 c.c. in excess, and note the amount taken.

Shake the flask to mix the contents, and add about 30 c.c. of 0·880 specific gravity ammonia liquor.

Make up to 500 c.c. with cold water.

Shake the flask to mix the contents.

Filter through a dry 20 cm. thick filter. Collect the filtrate in a clean beaker, and stir well.

Measure off 250 c.c. of the filtrate into a flask of about 600 c.c. capacity.

Add glacial acetic acid until just neutral. Much

of the success of the estimation depends on the accuracy with which neutralisation is effected.

Add 6 drops of dilute ammonia (1 of 0·880 specific gravity ammonia in 5 of water).

Dissolve 2 grammes of ammonium sulphate in the solution in the flask. This serves the double purpose of increasing the iodine turbidity, and retards the formation of a deceptive precipitate which is not readily soluble in small excess of potassium cyanide.* It also retards the formation of a nickel-molybdenum precipitate, if the latter is present.

From a burette, measure standard silver nitrate solution. Shake the flask while adding the silver nitrate. Cautiously continue the additions till a white cloud is formed which remains even after shaking the solution.

Some analysts prefer to overshoot the mark by adding excess of the standard silver nitrate solution, and then adding enough of the standard cyanide to clear the solution.

EXAMPLE OF CALCULATION.—1 gramme of sample dissolved, half of the solution titrated.

50 c.c. of standard cyanide solution used.

5·1 c.c. of standard silver nitrate required to give milkiness or cloud.

Multiply the No. of c.c. of the standard silver solution used by 2, add 10 per cent., and divide by 10. In this instance 5·1 × 2 + 10 per cent. = 11·22.

* Brearley and Jervis, *Chemical News*, 7th October, 1908.

Subtract from the No. of c.c. of standard cyanide used

$$50 - 11 \cdot 22 = 38 \cdot 78.$$

Now divide by 10: result, $3 \cdot 88$.

$3 \cdot 88 \doteqdot$ percentage of nickel in the sample of steel.

ESTIMATION OF NICKEL IN FERRO-NICKEL.

The portion of the sample taken for the estimation of nickel should be reduced to the finest possible state of division in an agate mortar.

Weigh off very accurately about $0 \cdot 25$ gramme of the finely-pulverised sample, and proceed with the estimation as directed in the preceding pages—using less, but not proportionately less, acid, &c.

ESTIMATION OF ARSENIC.

VOLUMETRIC ESTIMATION OF ARSENIC IN STEEL.—
FISCHER'S PROCESS, AS APPLIED BY STEAD.[*]

In this process there are three stages :—

    (1) Dissolving the weighed sample.
    (2) Distilling the solution.
    (3) Titrating the distillate.

The following apparatus is employed, viz. :—

For (1). A 600 c.c. (about 20-oz.) conical flask with a two-hole rubber cork, carrying a safety funnel and a delivery tube, also a Winkler's absorption apparatus, as shown in Fig. 20.

For (2). A distillation flask, Liebig condenser, and receiver with stands and tripod, as shown in Fig. 21.

Outline of the Process.—The weighed sample is transferred to the conical flask and dissolved in hydrochloric acid. While dissolving, gaseous compounds are evolved, including some arsenuretted hydrogen (AsH_3), which is converted into arsenious acid (H_3AsO_3), and absorbed in bromine water contained in the spiral of the Winkler absorption apparatus.

$$AsH_3 + 3H_2O + 3Br_2 = H_3AsO_3 + 6HBr.$$
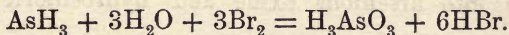
The excess bromine is boiled off, the remaining

clear solution and the solution left in the conical flask (in which most of the arsenic has been retained) are washed into the distillation flask and gently distilled.

On prolonged distillation of the solution, the ferrous chloride of which assists the distillation, all
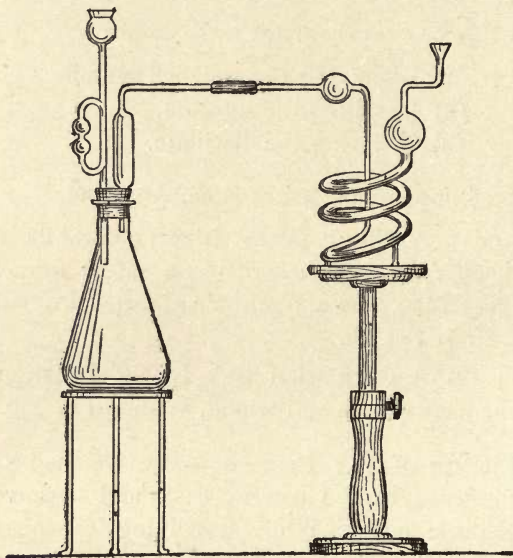
Fig. 20.—Apparatus used when dissolving steel containing arsenic.

the arsenic is conveyed to the receiver as arsenious chloride ($AsCl_3$) which in excess of water is decomposed into arsenious oxide and hydrochloric acid, thus—

$$4AsCl_3 + 6H_2O = As_4O_6 + 12HCl.$$
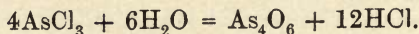
The distillate is neutralised with ammonia liquor,

made alkaline by the addition of sodium bicarbonate, starch solution is added to act as an indicator, and the arsenious oxide is titrated with standard iodine solution. The reaction may be represented by the equation—

$$As_4O_6 + 8NaHCO_3 + 4I_2$$
$$= 2As_2O_5 + 8NaI + 8CO_2 + 4H_2O.$$
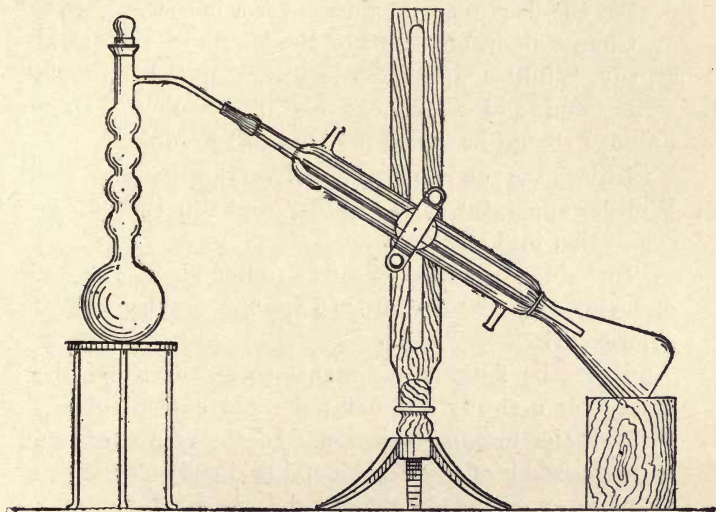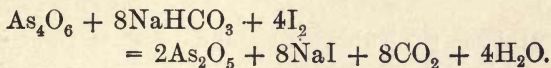
Fig. 21.—Apparatus used when distilling the solution from arsenical steel.

Iodine, added in excess, strikes a blue colour with the starch. From the quantity of standard iodine solution required to complete the reaction the amount of arsenic present is ascertained, and the percentage is calculated.

Details of the Process—Dissolving.—Weigh off 20 grammes of the sample, which should be in the form of fine turnings or drillings. (From 10 to 50 grammes may be weighed off.)

Transfer the weighed portion to the 20-oz. conical flask.

Moisten the rubber cork and press it tightly into the neck of the flask.

Set the flask on wire gauze over a burner.

Charge about one-third of the length of the spiral of the Winkler apparatus with saturated bromine water, and add about one c.c. of bromine. More bromine should be added if found to be required.

Bring the ends of the delivery tube and the Winkler apparatus close together, and slip the rubber connection into position.

Introduce through the safety funnel about 100 c.c. of water, and 120 c.c. of 1·16 specific gravity hydrochloric acid.

Heat the flask and contents so as to ensure the passage of a steady but not too rapid current of gas through the bromine solution. In the course of one hour the whole of the steel should be dissolved. When no more evolution of gas can be observed, boil the liquid in the flask so as to completely drive all the gas into and through the bromine solution.

Disconnect the Winkler apparatus and wash the solution into a 100 c.c. beaker.

Boil off the bromine.

Wash the clear solution into the distilling flask (Fig. 21).

Wash also the solution from the conical flask into

the distillation flask and close the neck with the stopper, or a tight-fitting cork.

Distilling.—Set the distillation flask on asbestos board over a burner, connect the flask to the condenser, adjust the latter and place a 300 c.c. (about 10-oz.) conical flask in a position as a receiver. Connect the water supply and cause a steady current of water to flow through the annulus of the condenser.

> While distillation is proceeding the strength of the standard iodine solution may be ascertained (see pp. 193 and 194).

Gently distil till the liquid remaining in the flask is reduced to about 10 c.c. **The distillation must not be forced; when finished, the distillate should be quite colourless and free from chloride of iron.**

Add about 20 c.c. of 1·16 specific gravity hydrochloric acid to the contents of the distillation flask.

Again distil till the liquid remaining in the flask is reduced to about 10 c.c.

Add about 20 c.c. of 1·16 specific gravity hydrochloric acid, along with about 5 c.c. of water.

Distil till the liquid left in the distillation flask measures about 20 c.c. At this point, as a rule, all the arsenic will have passed into the distillate, but it is advisable to make quite certain and to add another 20 c.c. of 1·16 specific gravity hydrochloric acid, along with about 5 c.c. of water, and distil to very small bulk.

Remove the receiver and add to the (colourless)

distillate in it two or three drops of litmus solution, and then a slight excess of ammonia liquor.

Add a few drops of 1·16 specific gravity hydrochloric acid—to more than neutralise the ammonia and leave the solution faintly acid.

Add solid sodium bicarbonate (acid sodium carbonate) in slight excess.

Cool the contents of the flask.

Add about 5 c.c. of clear, cold starch solution (see p. 416). Set the receiver on a white porcelain slab under the burette, and proceed with the titration as directed on pp. 191 to 195.

When dissolving steels in dilute hydrochloric acid, if there is no rust on the sample or ferric chloride present in the acid and the presence of air is carefully avoided, as a rule, only about one-tenth of the total arsenic passes off with the gas.

When solution is effected entirely in the cold a very much less quantity is evolved, and a very slight amount passes into the solution. As an example, an alloy containing 4·125 per cent. of arsenic dissolved in dilute hydrochloric acid in the cold gave the following results :—

Evolved as gas, .	0·035	per cent
Found in the solution,	0·125	,,
Remaining insoluble as a dense black residue,	3·965	,,
	4·125	,,

Alternative Method of Distilling.

The time occupied in distilling may be shortened by adopting the following modification :—

Transfer the weighed sample to the conical flask which has been fitted as shown in Fig. 20, p. 184.

Moisten the rubber cork and press it tightly into the neck of the flask.

Charge about one-third of the length of the spiral of the Winkler apparatus with saturated bromine water, and add about 1 c.c. of bromine.

Connect the Winkler apparatus to the delivery tube.

Introduce through the safety funnel about 100 c.c. of water and 120 c.c. of 1·16 specific gravity hydrochloric acid. This quantity should suffice for 25 grammes of sample.

Heat gently to hasten solution, and continue the heating till all the iron has been dissolved and only a little dark residue is left in the liquid in the flask.

Disconnect the apparatus.

Wash the bromine solution into a 250 c.c. beaker.

Boil off, gently, the bromine.

Wash the solution from the beaker into the conical flask.

Drop about half a gramme of zinc sulphide into the solution in the flask.

Shake the flask violently for about three minutes, so as to agitate the contents.

All the arsenic will then be in the insoluble state, partly as sulphide and partly as a black precipitate of, possibly, free arsenic and arsenide of iron.

Filter off through a 12·5 cm. smooth filter-paper Rinse the flask with cold distilled water.

Wash the precipitate and residue two or three times with water, then wash the solids into a beaker of about 150 c.c. capacity. If the precipitate should happen to stick pertinaciously to the filter, dissolve with bromine water and hydrochloric acid, and wash the filter carefully with hot water to remove all traces of arsenic.

Dissolve the washed precipitate in bromine water to which a little hydrochloric acid has been added.

Boil off, gently, the bromine.

Wash the solution from the beaker into the distilling flask shown in Fig. 21, p. 185.

Set the distillation flask on asbestos board over a burner, connect the flask to the condenser, adjust the latter and place a 300 c.c. (about 10-oz.) conical flask containing about 75 c.c. of water in position as a receiver. Connect the water supply and cause a steady current of water to flow through the annulus of the condenser.

Add about 15 grammes of solid ferrous chloride, or about 5 c.c. of the steel solution remaining after separating the arsenic during a previous estimation. The solution should contain about 10 per cent. of soluble iron as ferrous chloride.

Close the neck of the distillation flask with the stopper or a tight-fitting cork.

Distil gently. Continue the distillation till the mixture in the flask is almost dry.

When the flask has cooled, add 20 c.c. of 1·16 specific gravity hydrochloric acid and distil again.

Add 20 c.c. of 1·16 specific gravity hydrochloric acid and 5 c.c. of 10 per cent. ferrous chloride, and again evaporate to small bulk.

> While distillation is proceeding the strength of the standard iodine solution may be ascertained (see pp. 193 and 194).

Detach the distillation flask and wash the condenser out twice with water—First distillate.

To ensure the complete removal of the arsenic, pour 20 c.c. of 1·16 specific gravity hydrochloric acid into the distilling flask, connect the condenser, place a receiver in position, and distil again—Second distillate.

Remove the receiver. Add to the (colourless) distillate in the first receiver two or three drops of litmus solution and then a slight excess of ammonia liquor.

Add a few drops of 1·16 specific gravity hydrochloric acid—to more than neutralise the ammonia and leave the solution faintly acid.

Add solid sodium bicarbonate (acid sodium carbonate) in slight excess.

Cool the contents of the flask.

Add about 5 c.c. of clear, cold starch solution (see p. 416), and set the receiver on a white porcelain slab under the burette and proceed with the titration as directed.

Titrating.—Fill a clean burette with standard iodine solution for arsenic estimation (see p. 407) and run off the solution into a sink.

Nearly fill the burette with the standard iodine

solution, place an Erdmann's float in the burette and adjust to zero.

Measure the standard iodine solution into the flask containing the distillate. Shake vigorously during addition. Continue the additions till a permanent violet or blue colouration is produced.

Read off and note the quantity of standard iodine solution required.

Treat the distillate from the second receiver in the same manner, and add the result, if any.

A "blank" is carried out side by side with tests in exactly the same way from the commencement, using the same quantity of acids and reagents.

From the quantity of standard iodine solution required, deduct the correction for the "blank," and calculate the percentage of arsenic found.

The iodine solution should be carefully standardised, and restandardised frequently.

EXAMPLE OF CALCULATION.—20 grammes of sample were taken for the estimation, and, after making the correction for the "blank," 16·4 c.c. of the standard iodine solution (each c.c. of which = 0·000498 gramme of arsenic) were required to complete the reaction.

$$16·4 \times 0·000498 = 0·00817.$$

0·00817 gramme = weight of arsenic in 20 grammes of the sample.

To find percentage—

$$\frac{0 \cdot 00817 \times 100}{20} = 0 \cdot 00817 \times 5 = 0 \cdot 041.$$

$0 \cdot 041$ = percentage of arsenic in the sample of steel.

STANDARDISING THE IODINE SOLUTION FOR ESTIMATION OF ARSENIC.

The standard solution of pure arsenious oxide (prepared as directed on p. 401) is assumed to contain $0 \cdot 0005$ gramme of arsenic per c.c., and is used to find the strength of the standard iodine solution as prepared for the estimation of arsenic.

Fill a clean burette with standard solution of arsenious oxide and run off the solution into a sink.

Refill the burette and adjust the solution to zero.

Measure 30 c.c. of the solution into an 18 cm. (about 7-inch) porcelain basin, or into a suitable conical flask.

Add about 100 c.c. of water, a few drops of litmus solution, an excess of sodium bicarbonate, and about 5 c.c. of freshly-prepared but cold starch solution (see p. 416).

Fill a clean burette with standard iodine solution for arsenic estimation (see p. 407), and run off the solution into a sink. Nearly refill the burette, place an Erdmann's float in the solution, and adjust to zero.

Measure the standard iodine solution into the solution in the basin or the flask (stirring or shaking

13

the contents meanwhile) until a somewhat persistent violet colour appears, then add it carefully drop by drop (stirring or shaking after each addition) until a distinct violet colour remains for about a minute after one of the drops.

Read off and note the volume, less the correction or blank (see p. 195) of iodine solution used.

Estimate the amount of standard iodine solution required for 35 c.c. of the standard arsenious solution, note the result, less the blank, and compare with the previous titration. If the results are not fairly concordant titrate again, using 25 c.c. of the standard arsenious solution. When three good consecutive results have been obtained the mean may be accepted.

EXAMPLE :—

Standard Arsenious Solution.	Standard Iodine Solution.	Iodine Solution Equal to Arsenious Solution.
c.c.	c.c.	c.c.
30	30·2	1·0067
35	35·1	1·0029
25	25·2	1·0080
		Mean 1·0059

Then as each c.c. of the arsenious solution contained 0·0066 gramme of arsenious oxide (= 0·0005 gramme of arsenic), the value of each c.c. of the standard iodine solution was $\dfrac{0·0005}{1·0059} = 0·000497$ gramme of arsenic.

The date of standardising, strength of the solution and amount allowed for blank should be noted on a label on the bottle containing the standard solution. Such a solution should be kept in a dark cupboard.

Correction for Quantity of Standard Iodine Solution required to show Colour in the Solutions used.

In a 300 c.c. conical flask dissolve about 0·5 gramme of sodium bicarbonate in about 200 c.c. of water, and add about 5 c.c. of freshly prepared but cold starch solution (see p. 416).

Set the flask on a white porcelain slab or piece of filter-paper under the burette containing the standard iodine solution.

Measure, from the burette—stirring vigorously after the addition of each drop—standard iodine solution until a distinct violet colour appears and remains. The depth of colour should correspond to that usually found at the end of an ordinary titration. The amount of the blank should be deducted from the reading of the burette when standardising and when assaying.

PLATTEN'S METHOD.

" This method was described by Mr. Platten in a paper read before the Society of Chemical Industry on 16th April, 1894, and depends on the fact that when sulphide of arsenic (obtained by treating the arsenical distillate with sulphuretted hydrogen) is boiled with

pure water, it is decomposed into sulphuretted hydrogen, which escapes, and arsenious oxide, which remains in solution. This solution is then titrated with iodine in the usual way."

"If the steel or iron contains much arsenic, a smaller quantity, say 1 or 2 grammes, may be dissolved in nitric acid of 1·20 specific gravity and the solution evaporated to dryness, the residue being dissolved in hydrochloric acid, and the solution transferred to the retort, and distilled directly with ferrous chloride and hydrochloric acid, care being taken that the distillation is not forced, so as to avoid any of the iron solution passing over into the distillate." *

Gravimetric Method for the Estimation of Arsenic in Steel.

Weigh off 10 grammes of the sample.

Transfer the weighed portion to a 15 cm. (about 6-inch) porcelain basin.

Add 50 c.c. of 1·42 specific gravity nitric acid, along with 30 c.c. of water.

Evaporate to dryness and roast thoroughly.

Allow to cool.

Detach as much as possible of the roasted mass and transfer it to a distilling flask (Fig. 20, p. 185).

Add 100 c.c. of 1·16 specific gravity hydrochloric acid.

Add about 25 grammes of solid ferrous chloride.

Dissolve the residue on the basin by adding 25

* Stead, *Iron and Steel Institute Journal*, vol. ii., 1895.

c.c. of 1·16 specific gravity hydrochloric acid, and boiling.

Pour the solution into the flask.

Set the distillation flask on asbestos board over a burner, connect the flask to the condenser, adjust the latter, and place a 300 c.c. (about 10-oz.) conical flask containing about 75 c.c. of water in position as a receiver. Connect the water supply and cause a steady current of water to flow through the annulus of the condenser.

Distil gently. Continue the distillation till the mixture in the flask is almost dry. If the distillation has not been forced the distillate will be quite colourless.

Detach the distillation flask and wash the condenser out twice with water.

Remove the receiver and add to the distillate in it just enough ammonia liquor to make it neutral.

Acidify slightly but distinctly with hydrochloric acid.

Heat to 44° C.

Pass a current of sulphuretted hydrogen through the liquid for about twenty minutes.

Add about half a gramme of zinc sulphide to the solution.

Shake the flask vigorously for about three or four minutes.

Collect the precipitate on an 11 cm. Swedish or black ribbon filter.

Wash three times with cold water. Wash the precipitate down to the bottom of the filter.

Take away the beaker containing the filtrate and washings and place a 500 c.c. beaker under the funnel.

Pierce the filter, and with a warm solution of ammonia (1 of 0·88 specific gravity ammonia to 4 of water) wash the precipitate into the beaker.

Evaporate to one-fourth the bulk.

Add an equal bulk of nitric acid.

Again evaporate to small bulk.

Allow to cool.

Neutralise by adding ammonia liquor.

Filter, if necessary, into a 250 c.c. conical flask.

To the clear, warm liquid add, drop by drop, 10 c.c. of magnesia mixture (see p. 408).

Add 20 c.c. of 0·88 specific gravity ammonia liquor.

Cork the flask and shake it vigorously for two or three minutes. This should cause the precipitation of all the arsenic in the form of magnesium-ammonium arsenate [$Mg(NH_4) AsO_4. 6H_2O$].

When the precipitate has settled, filter into a 9 cm. Swedish filter.

Wash six or seven times with ammonia water— say 1 of 0·88 specific gravity ammonia liquor to 4 of water.

Dry the precipitate by placing the funnel, with filter-paper and contents, on a filter dryer (Fig. 4, p. 14), covering with paper, and allowing to dry thoroughly on the hot plate.

Open out the dried filter and detach as much as possible of the precipitate.

Transfer the precipitate to a tared porcelain crucible.

Place the filter-paper in another tared porcelain crucible, saturate the paper with strong ammonium nitrate solution; dry and ignite the paper, gently at first, and finishing in a muffle which is at a red heat. These precautions are taken to avoid reduction and volatilisation of arsenic.

Set the tared crucible containing the precipitate over a good Bunsen burner. By means of an ordinary tobacco pipe, the inverted bowl of which covers the crucible, convey a slow current of oxygen to the crucible. Gradually raise the temperature to bright redness. Continue the heating in an atmosphere of oxygen for ten minutes after the highest temperature has been attained. By careful ignition in an atmosphere of oxygen a residue of fixed composition may be obtained.

During ignition, the precipitate loses ammonia and water, and is converted into magnesium-pyroarsenate, $Mg_2As_2O_7$, thus—

$$2Mg(NH_4)AsO_4 . 6H_2O = Mg_2As_2O_7 + 2NH_3 + 7H_2O.$$
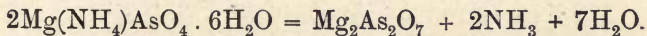
Allow the crucibles to cool in a desiccator, weigh, and note the weight.

Repeat the heating of the crucible which contained the precipitate in an atmosphere of oxygen.

Allow to cool in a desiccator.

Reweigh.

Repeat the ignition in oxygen, if necessary, until the weight becomes constant.

Calculate the percentage.

Example—

Weight of crucibles + ash	.	= 19·3819 grammes.
,,	crucibles .	.	= 19·3767 ,,
,,	ash and precipitate .	= 0·0052 gramme.
,,	filter ash .	.	= 0·0008 ,,
,,	precipitate ($Mg_2As_2O_7$) =	0·0044 ,,

The percentage of arsenic is calculated from the weight of pyroarsenate, which contains 48·272 per cent. of arsenic.

When 10 grammes of sample are operated on, the factor for ascertaining the percentage is—

$$\frac{48\cdot272}{10} = 4\cdot8272.$$

Log 4·8272 = 0·6836953.

0·0044 × 4·8272 = 0·021 = percentage of arsenic in the sample of steel.

Estimation of Arsenic in Pig Iron.

" In testing pig irons they may be dissolved in nitric acid and evaporated to dryness, or be treated in a flask with hydrochloric acid, as previously described, but if the latter method is adopted, it is advisable to distil without separating the arsenic as sulphide in the first instance." *

The gravimetric method described in the foregoing pages is also applicable to pig irons.

* Stead, *Iron and Steel Institute Journal*, vol. i., 1895.

ESTIMATION OF ARSENIC IN IRON ORES.

"In testing ores it is only necessary to place the ore directly into the retort, and distil at once with hydrochloric acid and ferrous chloride, taking care to place a few pieces of firebrick in the vessel, to avoid the 'jumping' of the liquid.

"If the ore contains much peroxide of manganese, it is advisable to dissolve it in a separate vessel to liberate and expel the chlorine, and then to transfer it into the retort.

"It is quite possible to accurately determine as small a quantity as 0·002 per cent. arsenic by this method." *

* Stead, *Iron and Steel Institute Journal,* vol. i., 1895.

ESTIMATION OF ALUMINIUM.

ESTIMATION OF ALUMINIUM IN STEEL.

Outline of the Process.—The weighed sample is dissolved in hydrochloric acid, the solution is evaporated to dryness, re-dissolved, and the silica separated. Ammonium phosphate is added to the solution, and a reaction takes place which may be represented by the equation—

$$Al_2Cl_6 + 2(NH_4)_2HPO_4 = 2AlPO_4 + 4(NH_4)Cl + 2HCl.$$
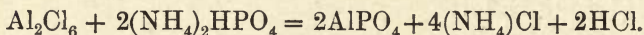
Sufficient ammonia liquor is then added to nearly neutralise the acid, and excess of sodium thiosulphate is added to reduce the iron to the ferrous condition and complete the neutralisation of the acid, thus—

$$2Fe_2Cl_6 + 2Na_2S_2O_3 = 4FeCl_2 + 4NaCl + S + 3SO_2$$
$$2HCl + Na_2S_2O_3 = 2NaCl + H_2O + S + SO_2.$$
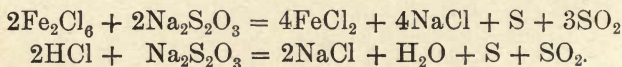
At this stage—the solution being neutral—all the aluminium is precipitated as phosphate on boiling. As this is accompanied by a small amount of ferric phosphate, the precipitate is collected on a filter, washed, and dissolved. The iron is precipitated by excess of sodium hydrate, and separated from the soluble aluminate of soda by fractional filtration.

From the filtrate the aluminium is again precipitated as phosphate, which is collected, washed, dried, ignited, and weighed. The percentage is then calculated.

NOTE.—The precipitates should be rapidly filtered as soon as ready, and quickly washed.

Details of the Process.—Weigh off a quantity of fine drillings, and note the weight taken. If the steel is supposed to contain about 0·01 per cent. of aluminium, 11 grammes of the sample may be weighed off.

Transfer the weighed drillings to a 600 c.c. broad Bohemian or Jena beaker.

Add 50 c.c. of 1·16 specific gravity hydrochloric acid.

Heat on a hot plate (see note on p. 377) till dissolved, and evaporate to dryness.

Add hydrochloric acid and hot water to the residue, and boil to dissolve the iron, &c.

If an insoluble residue (silica, &c.) is present, filter through a 12·5 cm. Swedish filter, and wash with a fine jet of water, collecting the filtrate and washings (which should not exceed 200 c.c.) in a 500 c.c. beaker.

Boil.

To separate the aluminium phosphate from the main bulk of the iron:

Add sufficient ammonium phosphate solution to precipitate all the alumina present at a subsequent stage of the estimation. 0·5 c.c. of 20 per cent. solution (or 5 c.c. of 2 per cent. solution) will precipitate all the alumina from 11 grammes of a sample containing not more than 0·07 per cent. of aluminium. If more aluminium than this is likely to be present a proportionately greater volume of phosphate solution must be added. But the phosphate must not be greatly in excess of the amount required to precipitate the aluminium, or too much ferric phosphate will be thrown down with it.

Add dilute ammonia solution till the free acid is neutralised. This point is readily known by a small precipitate of phosphates remaining insoluble after repeatedly shaking the solution.

Add hydrochloric acid, drop by drop, till the solution is clear.

Boil.

As soon as boiling commences add 50 c.c. of boiling saturated solution of sodium thiosulphate (see p. 415).

Continue the boiling till the solution does not give off sulphurous anhydride. If there is a doubt whether or not there is excess of thiosulphate, add a few more c.c. of the saturated solution, and if this does not give a precipitate of sulphur, sufficient thiosulphate has been added.

Test for sulphurous anhydride by holding a piece of filter-paper moistened with solution of dichromate or permanganate of potash in the vapour from the beaker.

While the solution is still very hot, filter the precipitate into a fluted 12·5 cm. Swedish filter, collecting the filtrate (and washings) in a 600 c.c. beaker.

Rinse out, with hot water, the beaker in which the precipitate was formed, but do not trouble to detach any firmly-adhering precipitate at this stage.

Wash the precipitate on the filter with hot water till free from all soluble iron and other salts. If the filtrate is slightly turbid on account of the presence of sulphur, the turbidity may be neglected.

Allow the precipitate to drain and then remove the beaker. The filtrate and washings are of no further use.

To separate the co-precipitated ferric hydrate :

Place a clean 400 c.c. beaker under the filter.

Warm 10 c.c. of 1·16 specific gravity hydrochloric acid, and 10 c.c. of water in the beaker in which the precipitation was effected, and pour the solution into the filter.

With a fine spout wash bottle wash with warm dilute hydrochloric acid (1 of 1·16 sp. gr. acid to 3 of water) till the whole of the phosphates are dissolved, and only a residue of sulphur is left on the paper. Wash again with the acid water and twice with hot water.

Evaporate the solution to a low bulk, and then transfer to a 7·5 cm. (about 3-inch) platinum or silver basin.

Place the basin over a water bath and evaporate to dryness.

Add about 3 grammes of pure sodium hydrate (caustic soda) prepared from sodium, and about 1 c.c. of hot water to partially dissolve it.

Heat gently over a Bunsen burner till evaporated to dryness, and afterwards more strongly till in a state of tranquil fusion.

Allow the basin and contents to cool.

Add about 50 c.c. of hot water, boil for about five minutes and allow to cool.

Transfer the liquid (containing soluble aluminate of soda and a precipitate of ferric hydrate) to a 110 c.c. graduated flask or measure.

Make up to the mark with cold water.

Mix the liquids well.

Pour into a dry double 12·5 cm. Swedish filter,

collecting 100 c.c. of the filtrate in a graduated flask. If the filtrate is turbid or cloudy it should be re-filtered.

Transfer the 100 c.c. of clear, filtered liquid to a 600 c.c. beaker.

To precipitate pure aluminium phosphate :

Add 4 c.c. of 20 per cent. ammonium phosphate solution.

Add dilute hydrochloric acid, little by little, till the precipitate which forms redissolves.

Make up with water to about 250 c.c.

Boil. As soon as the boiling commences add 25 c.c. of boiling saturated solution of sodium thiosulphate (see p. 415).

Boil for about half an hour. If the beaker bumps badly, it is advisable to pass in a stream of air while boiling.

Allow the precipitate to settle.

Decant off the clear liquid through a 15 cm. Swedish filter into a large clean beaker.

Add about 300 c.c. of boiling water to the precipitate in the beaker, allow to settle and again decant. This decantation should be performed at least three or four times, as the precipitate is difficult to wash.

Add more boiling water, and boil the large bulk of liquid before finally decanting through a 15 cm. Swedish filter.

Wash, with hot water, the precipitate into the filter.

Wash the precipitate in the filter with hot water, until the washings are free from chlorides.

Dry the precipitate by placing the funnel with

filter-paper and contents on a filter dryer (fig. 4, p. 14), covering with paper, and allowing to dry on the hot plate.

Place the dried residue and filter-papers in a tared platinum or porcelain crucible or capsule.

Ignite in a hot muffle.

Withdraw the crucible, or capsule, and contents, and allow to cool in a desiccator.

Weigh quickly and note the weight.

Calculate the percentage.

EXAMPLE—

					Grammes.
Weight of crucible + ash + precipitate			.	=	10·0447
„ crucible	.	.	.	=	10·0384
„ ash + precipitate	.	.	=		0·0063
„ filter ash	.	.	.	=	0·0008
„ precipitate ($AlPO_4$)	.	.	=		0·0055

The washed and ignited precipitate consisting of $AlPO_4$, contains 22·195 per cent. of aluminium.

$$\text{Log } 22\text{·}195 = 1\text{·}3462551.$$

Solution from 10 grammes was taken for the estimation.

$$\frac{0\text{·}0055 \times 22\text{·}195}{10} = 0\text{·}012,$$

0·012 = percentage of aluminium in the sample of steel.

Aluminium in pig iron may be estimated by the above method.

ESTIMATION OF COPPER IN STEEL.

GRAVIMETRIC ESTIMATION AS SULPHOCYANIDE OF
COPPER (BASED ON GUYARD'S METHOD).

Outline of the Process.—A weighed portion of
the sample is dissolved, the excess acids are neutralised,
and hydrochloric acid is added. Alkaline bisulphite is
then added to reduce the copper to the cuprous state—

$$2CuCl_2 + 2NaHSO_3 = Cu_2Cl_2 + 2HCl + Na_2SO_4 + SO_2.$$
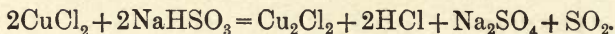
Incidentally ferric chloride is reduced to ferrous
chloride—

$$Fe_2Cl_6 + 2NaHSO_3 = 2FeCl_2 + 2HCl + Na_2SO_4 + SO_2.$$
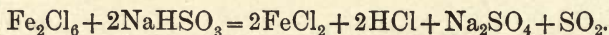
Ammonium thiocyanate (sulphocyanide) is added,
and the copper present is precipitated as cuprous
thiocyanate—

$$Cu_2Cl_2 + 2(NH_4)S(CN) = 2CuS(CN) + 2(NH_4)Cl.$$
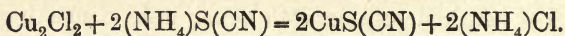
This precipitate is collected, washed, dried and
weighed. The percentage is then calculated.

Details of the Process.—Weigh off 10 grammes
of the sample and transfer to a 500 c.c. beaker.

Dissolve in the minimum amount of aqua regia
(see p. 403), and boil off excess of acids.

Add sufficient ammonia liquor to cause the forma-
tion of a permanent precipitate.

Add 20 c.c. of 1·16 specific gravity hydrochloric
acid.

Dilute to about 400 c.c. with water.

Reduce the copper (and incidentally the iron present) by means of a strong solution of sodium bisulphite.

Heat to about 60° C.

Add 5 c.c. of a 10 per cent. solution of ammonium thiocyanate. This will cause the formation of a white precipitate of cuprous thiocyanate [CuS(CN)] if copper is present—with perhaps a little sulphur.

Collect the precipitate on a 12·5 cm. Swedish filter, and wash well with warm water.

Take away the beaker containing the filtrate and washings, and place a 400 c.c. beaker in its place.

With a solution of one part of 0·88 specific gravity liquor ammonia to two parts of water dissolve the thiocyanate on the filter.

Wash well with more ammonia water.

Acidify the contents of the beaker with hydrochloric acid, then add about 2 c.c. more of the acid.

Heat to about 60° C.

Add about 2 c.c. of 10 per cent. thiocyanate solution.

Allow the precipitate to settle.

Collect on a 9 cm. smooth filter.

Wash well with warm water.

Wash the precipitate into a 7·5 cm. (about 3-inch) tared basin.

Allow to dry on a water bath.

Wipe the outside of the basin with a cloth which does not leave fluff.

Allow to cool in a desiccator.

Weigh, and calculate the percentage.

14

EXAMPLE—

	Grammes.
Weight of basin + precipitate . . . =	23·4678
„ basin only . . . . =	23·4625
„ precipitate . . . . =	0·0053

The washed and dried precipitate contains 52·28 per cent. of copper, and when 10 grammes of sample have been taken for the estimation the factor for calculating is 5·228.

Log 5·228 = 0·7183356.

0·0053 × 5·228 = 0·0277 = percentage of copper in the sample of steel.

Mr. John E. Stead gives * the following method :—
The alloy was dissolved in the least possible quantity to effect solution of nitro-hydrochloric acid, and when this was complete the solvent acids were removed by heating with strong sulphuric acid. The copper was separated by hydric sulphide, and the iron determined in the filtrate by a standard bichrome solution. The sulphides were dissolved in nitric acid, and the copper determined volumetrically by the iodine method, a method which has been found by long experience to give quite as accurate results as the most refined electrolytic methods.

* *Iron and Steel Institute Journal*, 1901, II., p. 110.

ESTIMATION OF TUNGSTEN IN STEEL.

Outline of the Process.—The weighed portion of the sample is treated with acids to effect decomposition. On continued heating, followed by dilution, tungstic oxide, accompanied by a little silica and ferric oxide, separates out. The solids are washed on a filter, dried, ignited, and weighed. The silica is carried off on treatment with hydrofluoric acid, the residue is fused with sodium carbonate, and the resulting sodium tungstate is dissolved and separated by filtering and washing. The dried insoluble residue is weighed. From the difference shown by the weighings the amount of tungstic oxide is ascertained, and the percentage of tungsten is calculated.

Details of the Process.—Weigh off 2 grammes of the sample.

Transfer the weighed portion to an 11·5 × 10 cm. (about 4½ × 4 inches) Bohemian or Jena beaker.

Add 50 c.c. of 1·16 specific gravity hydrochloric acid.

Cover the beaker with a clock glass, and heat nearly to boiling.

Add, not more than three or four drops at a time, 1·42 specific gravity nitric acid, allowing the frothing to subside completely before a further quantity is added. By the use of such a large excess of hydrochloric acid (which, although hot, is kept as concentrated as possible) the steel may be decomposed

by adding very little more nitric acid than is necessary to oxidise the iron without causing (and this is important) any separation of tungstic oxide. When complete decomposition has been effected, the iron should be in the ferric condition, and a black film of carbonaceous matter will have separated.

When decomposition has been completed, boil the liquid briskly to about one-third of its bulk. During the boiling a considerable amount of the tungstic oxide should separate out.

In the event of separation of tungstic oxide before complete decomposition of the drillings has been effected, the latter are protected from the attack of the acids, and the amount of the impurity in the separated residue is very much larger than is desirable.

Dilute with about 60 c.c. of hot distilled water.

Boil for a minute or two.

Filter, using a 12·5 cm. Swedish filter.

After transferring the tungstic oxide, so far as possible, to the filter, it will be found that in every case a film remains on the side of the beaker which defies removal by a "policeman." A small piece of ashless filter-paper, soaked with a drop or two of ammonium hydrate, readily brings it away, and the filter-paper is then ignited along with the main residue.

Wash the precipitate on the filter several times with hot water slightly acidulated with hydrochloric acid.

Place the funnel with filter-paper and contents on a filter dryer (Fig. 4, p. 14), cover with paper, and allow to dry on a hot plate.

Place the filter-paper with the dried residue in a platinum capsule, and ignite in a muffle furnace or over a Bunsen burner.

After ignition, add a few drops of pure hydrofluoric acid and a drop of sulphuric acid.

Cautiously remove the acid by evaporation and then heat the capsule and contents at a full red heat for a few minutes. This treatment eliminates the silica as (gaseous) silicon tetra-fluoride (SiF_4).

Allow the capsule and residue to cool.

Weigh, and note the weight of the capsule and contents.

Cover the powder in the capsule with 2 or 3 grammes of dry sodium carbonate, and place in a muffle furnace.

When complete fusion has taken place, withdraw the capsule, agitate it so as to mix the contents, allow to cool, add about 50 c.c. of water, and boil gently for a few minutes. The tungstic oxide will be dissolved.

Filter, using a 12·5 cm. Swedish filter. Collect the filtrate (and washings) in a beaker; if yellow, estimate the chromium present, as directed on p. 147.

Wash the residue on the filter several times with warm water.

Place the funnel with the filter-paper and washed residue (ferric oxide) on a filter dryer, cover with paper, and allow to dry on the hot plate.

Place the dried residue and filter-paper in the platinum capsule which had been used for the previous ignition, and ignite in a muffle furnace or over a Bunsen burner.

Allow to cool.

Weigh the capsule and residue, and note the weight.

The difference between the first and second weighings gives the weight of the tungstic oxide (WO_3).

Calculate the percentage.

EXAMPLE—

Grammes.

Weight of capsule + tungstic oxide + ferric
    oxide, &c. .   .   .   .   .   . $= 17\cdot4895$
After dissolving the tungsten compound—
    weight of capsule + ferric oxide, &c.
    + filter ash   .   .   .   .   . $= 17\cdot1222$

Weight of tungstic oxide .   .   .   . $= \ \ 0\cdot3673$

Tungstic oxide (WO_3) contains $79\cdot31$ per cent. of tungsten, and when 2 grammes of sample are taken for the estimation the factor for calculation is—

$$\frac{79\cdot31}{2} = 39\cdot655.$$

Log $39\cdot655 = 1\cdot5982980.$

$0\cdot3673 \times 39\cdot655 = 14\cdot57 =$ percentage of tungsten in the sample.

The filtrate and washings collected after the fusion with sodium carbonate contain the whole of the tungsten as sodium tungstate, and (if yellow) small quantities of chromium as sodium chromate. A very large number of assays by Ibbotson convinced him

that the determination of the chromium in the tungstic oxide residue may, for all practical purposes, be neglected, as its amount very nearly counterbalances the 2 or 3 milligrammes of tungstic oxide left in the solution when the evaporation of the original solution of the steel is not conducted far beyond the point at which tungstic oxide first falls out. If, however, it be considered necessary to determine the amount of the latter, the filtrate is acidulated with sulphuric acid, a slight excess (5 to 10 c.c.) of decinormal ferrous ammonium sulphate solution is added, and the excess of the latter titrated. The amount of chromic oxide found is deducted from the weight of the tungstic oxide.

ESTIMATION OF VANADIUM.

ESTIMATION OF VANADIUM IN IRON AND STEEL.

The following ingenious method by PROFESSOR EDWARD DE MILLE CAMPBELL and EDWIN LE GRAND WOODHAMS, taken by permission from the *Journal of the American Chemical Society*, August, 1908, introduces the application of two novel ideas in analytical practice : (*a*) the separation of iron, as sulphate, in alcohol, and (*b*) the reduction of one of the elements when fused.

Outline of the Process.—The weighed portion of the sample is dissolved in dilute sulphuric acid, and the insoluble portion (which usually contains about half of the vanadium) is separated on filtering. The filtrate is evaporated to small bulk, and hydrogen sulphide is passed in to reduce ferrous sulphate and to precipitate any arsenic and copper which may be present. The liquid is boiled to reduce the bulk and to drive off excess of hydrogen sulphide, cooled, alcohol added, and the whole shaken at frequent intervals to further the precipitation of the iron as ferrous sulphate. This is separated on a filter. The filtrate and washings are collected, and, after addition of hydrogen peroxide to peroxidise the small amount of ferrous sulphate, is boiled, and sodium carbonate is added to precipitate the iron, chromium, manganese, and vanadium. The precipitate is washed and dried,

placed in a platinum crucible along with the insoluble residue, and, after ignition, is fused with sodium carbonate. Charcoal powder is added to the melt, and fusion is continued. This treatment enables a sharp separation of chromium from vanadium to be effected on subsequent treatment with hot water, and filtering. The filtrate and washings, now containing all the vanadium, are acidified, and, after addition of permanganate solution, boiled, sulphur dioxide added, and again boiled. The whole is then evaporated till fumes come off freely, cooled a little, diluted, and titrated with standard potassium permanganate solution.

Details of the Process.—Weigh off 5 grammes of the sample.

Transfer the weighed portion to a 250 c.c. conical flask.

Add 30 c.c. of water and 14 c.c. of 1·51 specific gravity sulphuric acid (prepared by pouring concentrated sulphuric acid into an equal volume of water).

Cover the flask with an inverted porcelain lid, and maintain at the boiling point till action ceases.

Filter through a 12·5 cm. Swedish filter, and wash the insoluble residue with hot water, collecting the filtrate and washings in a 250 c.c. conical flask.

> Place the drained residue and filter in a platinum crucible, char at a low red heat, and burn off the carbon from the filter-paper. Keep the capsule and residue till required.

Boil the filtrate down to about 50 c.c.

Pass in hydrogen sulphide for five minutes to reduce any ferric sulphate to ferrous sulphate and to precipitate copper and arsenic, if present.

Cover the flask with an inverted porcelain lid, and boil the solution down to about 35 c.c. This boiling should remove the excess of hydrogen sulphide.

Cool the flask under a water tap to the temperature of the room. If the volume is not reduced below 35 c.c., no ferrous sulphate will crystallise out upon thus cooling.

After cooling, rotate the flask and add gradually 100 c.c. of ordinary ethyl alcohol. The amount of alcohol added should be at least three times the volume of the ferrous sulphate solution. Denatured alcohol seems to give as good results as the pure ethyl alcohol.

After adding the alcohol, stopper the flask, cool if not perfectly cold, and shake at frequent intervals for five or ten minutes to complete the precipitation of nearly all the iron as ferrous sulphate.

Filter through a 15 cm. Swedish filter. Wash with alcohol diluted with one-third its volume of water, collecting the filtrate and washings in a conical flask. If moderate suction is used (see p. 381) the crystallised salt is very thoroughly and easily washed.

Rinse the filtrate and washings into a 600 c.c. beaker, using 100 c.c. of water for this purpose.

Add 15 or 20 c.c. of hydrogen peroxide in order to oxidise the small amount of ferrous sulphate still in the solution.

Bring the solution to a boil. and then to this nearly boiling solution add sodium carbonate until

there is a slight but distinct alkaline reaction of litmus.

Keep the solution at the boiling point for ten or fifteen minutes until the precipitate, which contains all the iron, chromium, manganese, and vanadium, has turned darker in colour and has become flocculent. Filter, and wash thoroughly with a hot 0·5 per cent. solution of sodium carbonate in order that all the soluble sulphates may be washed out.

Dry the precipitate.

Place the dried precipitate in the platinum crucible containing the ignited residue, cover the crucible, char the filter at a low heat, then remove the cover and complete the ignition.

Allow the crucible to cool.

Add 5 grammes of sodium carbonate, mix thoroughly with the ignited precipitate, and fuse for fifteen or twenty minutes in the covered crucible. The fusion should be carried on carefully to avoid spattering, and the heat should not be raised above a moderate red, or just enough to keep the sodium carbonate fluid.

After fusing for fifteen or twenty minutes with the sodium carbonate alone, remove the cover from the crucible, add 0·3 or 0·4 gramme of powdered charcoal, replace the cover and raise the heat to a moderate red, or just sufficient to maintain fluidity, for ten minutes longer.

Cool, and extract the fused melt with 25 or 30 c.c. of hot water.

By fusing with sodium carbonate alone, the vanadium will be converted into the soluble sodium vanadate, but part of the chromium, which is usually present in special steels, will be

oxidised to sodium chromate. The addition of charcoa and the continuation of the fusion for ten minutes reduces the sodium chromate to chromic oxide, but does not affect the extraction of the vanadium, so that a very sharp separation of chromium is obtained.

When the disintegration of the melt is complete, filter and wash well with hot water. The filtrate will contain all of the vanadium, but no chromium. The filtrate should be either colourless or slightly tinged with yellow, due to the presence of sodium sulphide, if the sulphates were not completely washed out of the precipitate obtained with sodium carbonate.

Add to the filtrate and washings 20 c.c. of 1·51 specific gravity sulphuric acid (see p. 417).

Boil the solution, and run in 3 or 4 c.c. of a 3 per cent. solution of potassium permanganate.

Boil for five minutes more.

Run in sulphur dioxide until all the potassium permanganate is reduced to manganous sulphate and the solution has turned blue from the reduction of the vanadic acid to divanadyl sulphate.

Evaporate the solution until fumes of sulphuric anhydride begin to come off freely.

Cool the solution and dilute with water to about 60 c.c., and titrate the warm solution with $\frac{N}{20}$ potassium permanganate.

If the excess of potassium permanganate is added, and the solution boiled down before reduction with sulphur dioxide, and then the excess of the sulphur dioxide destroyed by evaporating to sulphur anhydride fumes, and the warm diluted solution titrated, at about 50° C., the oxidation of the divanadyl sulphate to vanadic acid is rapid and the end reaction sharp.

Since the oxidation of the vanadium is from V_2O_4 to V_2O_5, the hydrogen equivalent of elemental vanadium must be the atomic weight of vanadium, and 1 c.c. of $\frac{N}{20}$ permanganate is equivalent to 0·00256 gramme of elemental vanadium.

Estimation of Vanadium in Steel—Volumetric Method.

From a Memo. by J. Kent Smith, American Vanadium Co.,
Pittsburg, Pa., U.S.A.

Mr. J. Kent Smith has investigated very fully the general methods for estimating vanadium in steels, &c. Those generally published are utterly unfit for works use, and often prove that they are not as correct as they should be. He has devised many methods based on the well-known reactions of vanadium and checked them synthetically in various ways. He claims no originality for either of the methods, which are based on the simplest laws of common-sense analysis, but they are giving very satisfactory results, and have stood comparison with many elaborate methods.

Details of the Process.—Weigh off 4 grammes of the steel, and dissolve in 48 c.c. of water and 12 c.c. of strong sulphuric acid.

When dissolved, oxidise with nitric acid, not using a great excess.

Evaporate to dryness on a hot plate.

Take up with 150 c.c. of water, and boil till dissolved.

Add 10 c.c. (or excess) of a $2\frac{1}{2}$ per cent. permanganate solution, and boil for five minutes.

Add a little manganese sulphate to precipitate any undecomposed permanganate.

Cool, and make up to half a litre with water.

Filter through a dry paper and take 375 c.c. of the clear filtrate (equals 3 grammes of steel).

Add 50 c.c. of dilute sulphuric acid.

Add a measured excess of $\frac{N}{10}$ ferrous sulphate (20 c.c. is enough for a steel containing $1\frac{1}{4}$ per cent. chromium), and titrate back with $\frac{N}{10}$ permanganate till permanently pink.

The equivalent of $\frac{N}{10}$ permanganate used up equals chromium (1 c.c. $= 0\cdot001743$ gramme of chromium).

Now add 1 or 2 c.c. of ferrous sulphate solution to dissolve any MnO_2 that may have been formed, and add permanganate *very gradually* until the solution is just pink. Just discharge this pink with $\frac{N}{20}$ ferrous sulphate.

> NOTE.—On the exact carrying out of this manipulation depends the accuracy of the vanadium estimation. With a little practice a fair manipulator should have no difficulty in hitting the point to a drop.

Next add a carefully measured 5 c.c. or excess of $\frac{N}{20}$ ferrous sulphate, and titrate back with $\frac{N}{20}$ dichromate solution and ferricyanide.

The equivalent quantity of dichromate used up equals vanadium (1 c.c. $\frac{N}{20}$ dichromate $= 0\cdot00256$ gramme vanadium).

EXAMPLES OF CALCULATION—

CHROMIUM.

20 c.c. ferrous sulphate used (approximately $\frac{N}{10}$).
Original ferrous sulphate 20 c.c. $= 21\cdot2$ c.c. $\frac{N}{10}$ $KMnO_4$.
$\frac{N}{10}$ $KMnO_4$ to bring back . $= 5\cdot6$ c.c.
Equivalent of $\frac{N}{20}$ $KMnO_4$ to
    chromium . . . $= 15\cdot6$ c.c.

$$\frac{15\cdot6 \times \cdot001743 \times 100}{3} = 0\cdot906 \text{ per cent. Cr.}$$

VANADIUM.

5 c.c. ferrous sulphate used (approximately $\frac{N}{20}$).

Original $FeSO_4$ used . . $= 5 \cdot 4$ c.c. $\frac{N}{20}$ dichromate.

$\frac{N}{20}$ $K_2Cr_2O_7$ to bring back . $= 3 \cdot 0$ c.c.

Equivalent of $\frac{N}{20}$ $K_2Cr_2O_7$ to

vanadium . . . $= 2 \cdot 4$ c.c.

$$\frac{2 \cdot 4 \times \cdot 00256 \times 100}{3} = 0 \cdot 204 \text{ per cent. vanadium.}$$

ESTIMATION OF VANADIUM IN ORES AND ALLOYS.

VOLUMETRIC METHOD.

Take 0·512 gramme of the finely powdered sample, and, in the first case, dissolve in dilute nitric acid, in the second in aqua regia, digesting in a warm place only.

To the solution add excess of strong sulphuric acid, and evaporate till copious fumes are evolved.

Dilute the liquid with water at about 30° C.

Add permanganate till just pink, and the "neutral" point has been attained as before.

Add a measured excess of $\frac{N}{10}$ ferrous sulphate, and titrate the excess with $\frac{N}{10}$ dichromate (1 c.c. = ·00512 gramme vanadium).

The equivalent c.c. of $\frac{N}{10}$ dichromate due to vanadium represents the percentage of vanadium.

EXAMPLE—

    0·512 gramme alloy used.

    $FeSO_4$ added.

50 c.c.	= 51·7 c.c. standard $\frac{N}{10}$ $K_2Cr_2O_7$.
Excess $FeSO_4$	= 12·5	,, ,,

Vanadium equivalent, 39·2   ,,   ,,

       = 39·20 per cent. vanadium.

N.B.—In oxides, &c., the vanadium percentage divided by 0·5614 equals the percentage of V_2O_5.

NOTES.—In the cases of ores and alloys difficultly soluble, a very convenient way to bring the vanadium into solution is to fuse the ore or alloy in a nickel or iron crucible with about eight times its weight of sodium peroxide, dissolving the melt in water, boiling, acidifying with sulphuric acid, and proceeding as usual.

Difficultly soluble alloys may also be readily dissolved by covering the finely floured alloy in a platinum dish with 15 c.c. HNO_3 (1·2 sp. gr.), and 20 c.c. dilute H_2SO_4 (1 to 3), letting as much as will dissolve on heating, and then adding about 2 c.c. of HF, and smoking off to sulphuric fumes. The solution is diluted, "neutralised," and titrated as usual.

The clarity of the end reaction is much enhanced, and the attainment of the "neutral point" is rendered much easier by having the solution well acid with sulphuric acid.

Care should be taken that the ferricyanide spot

15

indicator is freshly prepared, and that it is quite free from ferrocyanides; the crystals of ferricyanide should be rough washed before dissolving them.

ESTIMATION OF VANADIUM IN STEEL.

COLORIMETRIC METHOD.

This method will be found to be of particular use where large numbers of steel assays have to be run through regularly. It depends upon a well known chemical reaction, and calls for the employment of Stead's chromometer with tubes graduated to 100 c.c. capacity.

A standard steel of known vanadium content, and somewhat similar to the sample worked upon, should be used; or a standard can be made by dissolving a plain steel containing no vanadium, adding to the solution known amounts of vanadium in standard vanadium solution, of chromium in the form of standard dichromate solution, or of nickel in the form of standard nickel-ammonium-sulphate solution.

Details of the Process.—Weigh off 1 gramme of the standard and of each of the samples. Transfer each weighed portion to a 12·2 × 9·7 cm. (about 4¾ × 3¾ inches) Jena or Bohemian beaker with a distinctive mark on each.

Add 50 c.c. of 20 per cent. nitric acid.

Boil till dissolved.

Cool the solutions.

Add 2 grammes of sodium bismuthate to each, and stir briskly.

Filter, collecting the filtrate (and washings) from the sample to be tested in the glass cylinder of the chromometer.

Wash twice with cold water.

Cautiously add solution of sulphurous anhydride till the liquid is decolourised.

Add 30 c.c. of 3 per cent. hydrogen peroxide solution.

Make up with water to 75 c.c.

Treat the filtrate (and washings) from the standard in the same way, and proceed to compare in the chromometer.

The percentage of vanadium is deduced by inverse proportion from the respective lengths of the columns of standard and sample.

Hydrogen peroxide imparts a mahogany colour to solutions containing vanadium, which deepens on standing—the standard and samples, however, should be " peroxidised " at the same time, and it is a matter of no moment whether the colour is "developed" in the beaker or the chromometer tube.

Titanium would interfere with the estimation.

ESTIMATION OF MOLYBDENUM.

ESTIMATION OF MOLYBDENUM IN STEEL.

Outline of the Process.—A weighed portion of the sample is treated with acids so as to dissolve the sample and cause the formation of insoluble tungstic oxide, which is separated on a filter from the other constituents. Sodium hydrate solution is added to the filtrate in quantity sufficient to neutralise the free acid but not to cause precipitation. The filtrate is then run cautiously into excess of hot sodium hydrate solution. By this means molybdenum is held in solution while the other constituents, except a little chromium, are precipitated. The precipitate is collected and washed. Lead acetate and ammonium acetate solutions are added to the filtrate and washings in order to precipitate the molybdenum as lead molybdate. This is filtered off, washed, dried, ignited, and weighed.

Details of the Process.—Weigh off 2 grammes of the sample, which should be in the form of fine drillings or turnings.

Transfer the weighed portion to a 600 c.c. Bohemian or Jena beaker.

Add 50 c.c. of 1·16 specific gravity hydrochloric acid.

Cover the beaker with a clock glass and heat nearly to the boiling point.

Add, a few drops at a time, 1·42 specific gravity

nitric acid. This causes a frothing, which should be allowed to subside before adding more. By the use of such a large excess of hydrochloric acid (which, although hot, is kept as concentrated as possible) the steel may be decomposed by adding very little more nitric acid than is necessary to oxidise the iron, without causing (and this is important) any separation of tungstic oxide. When complete decomposition has been effected, the iron should be in the ferric condition, and a black film of carbonaceous matter will have separated.

The solution, which has been maintained below boiling point, should now be boiled.

Evaporate as rapidly as possible to very low bulk, but not beyond pastiness.

Add a mixture of 40 c.c. of hot water, and 15 c.c. of 1·16 specific gravity hydrochloric acid.

Boil for two or three minutes.

Pour the solution, now containing a precipitate of tungstic oxide, into a 12·5 cm. Swedish filter. Wash well with water slightly acidulated with hydrochloric acid, collecting the filtrate and washings in a 300 c.c. conical flask.

The washed precipitate, if not too cumbersome, may be weighed, &c., for the estimation of tungsten (see p. 215 for notes on precautions).

To the filtrate add solution of sodium hydrate, shaking the flask well during and between each addition, until the free hydrochloric acid is neutralised. This occurs before the formation of a permanent precipitate, or even of a pronounced darkening of colour. It is important, in order to avoid a partial

precipitation of the molybdenum as basic ferric molybdate, to stop the neutralisation with caustic alkali before the darkening in colour takes place.

Transfer the solution (which with the washings should not exceed 350 c.c.) to a separating funnel.

Dissolve not less than 7 grammes of sodium hydrate in 150 c.c. of water in a 500 c.c. graduated flask, and heat the solution nearly to boiling point.

Run the solution in the separating funnel in a stream of rapid drops into the hot solution in the graduated flask, shaking the flask vigorously all the time.

By thus adding the partially neutralised mixture to the excess of caustic alkali, instead of operating in the converse manner, the molybdenum is held in solution as sodium molybdate. The iron and nearly all the chromium are precipitated as hydrates, but a small amount of the latter metal invariably passes into solution as sodium chromate.

Prepare a 28 cm. (about 11-inch) folded filter of No. 598 C. S. & S. or other thick filter-paper, set it in an 18 cm. (about 7-inch) funnel, saturate it with hot water, and place in a large filter stand (see Fig. 7, p. 36). Allow the superfluous water to drain off.

Fill up the 500 c.c. flask to the containing mark with warm water. Close it with the stopper and mix the contents well.

Place a 250 c.c. graduated flask under the funnel.

Pour from the 500 c.c. flask into the filter, and

collect 250 c.c. of the clear filtrate. This represents 1 gramme of the sample.

Transfer the measured quantity to a 500 c.c. beaker.

Acidify with hydrochloric acid, using methyl orange as an indicator.

Add 5 c.c. more of 1·16 specific gravity hydrochloric acid. This excess is added to correct a tendency to the contamination of the lead molybdate (to be subsequently precipitated) with basic compounds.

Add sulphurous acid (see p. 418) to reduce the small amount of sodium chromate which is usually present.

Boil.

Add 40 c.c. of ammonium acetate solution (see p. 401). This not only substitutes free acetic acid, in which lead molybdate is insoluble, for the free hydrochloric acid, but serves to prevent the precipitation of lead sulphate.

Add 6 c.c. of lead acetate solution (see p. 408).

Collect the precipitate of lead molybdate in a 12·5 cm. Swedish filter.

Wash with hot water.

Place the funnel with filter-paper and contents on a filter dryer (Fig. 4, p. 14), cover with paper and allow to dry on a hot plate.

Ignite in a tared porcelain capsule. Prolonged ignition at a high temperature is not harmful.

Allow to cool in a desiccator.

Weigh and note the weight.

EXAMPLE—

		Grammes.
Weight of crucible + ash + precipitate	=	17·0362
„ crucible	=	16·9123
„ ash + precipitate . . .	=	0·1239
„ ash	=	0·0008
„ precipitate	=	0·1231

The pure cream-coloured, ignited precipitate of $PbMoO_4$, contains 26·15 per cent. of molybdenum, and when half of the solution from 2 grammes has been precipitated, washed, dried and ignited, the factor for calculating the percentage is 26·15.

Log 26·15 = 1·4174717.

0·1231 × 26·15 = 3·219 = percentage of molybdenum in the sample of steel.

NOTES.*—The estimation of molybdenum in steel as carried out by this process is not interfered with by any of the usual elements found in steel, such elements being either precipitated along with the iron or exerting no influence in the subsequent precipitation of the molybdate with lead acetate: this remark, of course, does not apply to tungsten.

* Ibbotson and Brearley, *Chemical News*, 8th June, 1900.

Results of Experiments Instituted by Ibbotson and Brearley to determine whether molybdenum in steel interferes with the estimation of the other elements, and how its interference may be overcome :—

Silicon.—Molybdenum does not interfere.

Manganese.—If estimated by separation of the iron with ammonium acetate and precipitation with bromine and ammonia, molybdenum exerts no influence. Unless a large excess of acetate is used, nearly all the molybdenum is precipitated with the iron.

Sulphur.—The gravimetric estimation of sulphur is accurate if the barium chloride is added to a distinctly acid solution in order to eliminate the possibility of contamination with $BaMoO_4$, or basic ferric molybdates. The evolution method—*i.e.*, the dissolution of the steel in hydrochloric acid, the evolved sulphuretted hydrogen being passed through metallic solutions—is also uninfluenced by the presence of molybdenum. One would expect low results due to the formation of MoS_3. This does not seem to be the case when strong hydrochloric acid is used to effect decomposition.

Phosphorus.—The rapid method, in which the phosphorus is precipitated in the presence of all the iron, gives high results, apparently in consequence of contamination of the yellow precipitate with

MoO_3. The difficulty may obviously be overcome by dissolving out in ammonia and precipitating with magnesia mixture.

Carbon.—The carbonaceous residue, after decomposing the sample with copper solutions, gives blue washings (Mo_3O_8) long after the copper salts have been washed out. The results, compared with direct combustions with PbO_2 or Pb_3O_4, are a few hundredths per cent. too low.

Iron.—On precipitating with ammonia, part of the molybdenum accompanies the iron; gravimetric results are, therefore, too high. The iron cannot be estimated by simply dissolving the sample and titrating, because the molybdenum, reduced by the liberated hydrogen to Mo_2O_3, falsifies the result by being oxidised to MoO_3. For a like reason ferric solutions containing molybdenum should not be reduced with zinc or stannous chloride. They may, however, be reduced with sulphurous anhydride, and titrated accurately either with bichromate or permanganate. Potassium ferro-cyanide does not certainly indicate ferric iron, on account of the very ready formation of a deep brown precipitate with MoO_3 solutions.

ESTIMATION OF MOLYBDENUM IN CAST IRON.

Proceed as directed for steel in the foregoing pages.

Where tungsten in considerable amount was present, Brearley and Ibbotson found it advantageous to filter off the graphite, burn the filter at low redness, and fuse the residue with potassium nitrate.

ESTIMATION OF MOLYBDENUM IN FERRO-MOLYBDENUM AND FUSED MOLYBDENUM.

These alloys are readily attacked by acids, and molybdenum may be estimated as directed in the foregoing pages.

The Estimation of Vanadium, Molybdenum, Chromium, and Nickel in Steel.

The method here detailed gives the result of successful investigation and discovery by Mr. Andrew A. Blair, and is taken, by permission, from the *Journal of the American Chemical Society*, August, 1908.

Details of the Process.—Dissolve 2 grammes of the sample in nitric acid with the addition of hydrochloric acid if necessary, evaporate to dryness, re-dissolve in hydrochloric acid, and evaporate until the solution is syrupy. Dissolve in a small amount of hydrochloric acid of 1·1 specific gravity, cool in ice cold water, and wash into a separatory funnel of about 250 c.c. capacity with as small an amount as possible of acid of the same strength. The separatory funnel should be conical in shape, and should be fitted at the lower end with a Geissler stop-cock, and at the upper end with a glass stopper. Both stopper and stop-cock should be most carefully ground to prevent leakage. Add to the solution in the funnel about 80 c.c. of ordinary ether, and shake vigorously for half a minute. An ordinary clamp with cork-lined jaws, supported on a stand, makes a convenient arrangement for holding the funnel. When the two strata have separated, open the stop-cock and allow the lower to run into another separatory funnel. Remove the stopper, wash the solution down with about 10 or 15 c.c. of hydrochloric acid of 1·1 specific gravity, shake again, and allow the washings to run

into the other funnel. Add 50 c.c. of ether to the solution in the second funnel to remove as much of the remaining iron as possible, run the acid solution into a beaker, and evaporate nearly to dryness. Add nitric acid in excess, and evaporate until all the hydrochloric acid is expelled, and finally, when the solution is almost syrupy, add 20 c.c. of hot water. Heat the solution, and add a few drops of sulphurous acid to reduce any chromic acid that may have been formed. Boil and pour the solution slowly, stirring vigorously, into a boiling solution of sodium hydroxide containing 100 grammes sodium hydroxide to the litre. Boil the solution for a few minutes, allow the precipitate to settle, filter, wash twice by decantation and finally on the filter until the filtrate measures about 300 c.c. in volume. The precipitate consists of the oxides of chromium, nickel, and iron, with the greater part of the manganese and any copper that may have been in the sample. The filtrate contains the vanadium, some silica and alumina from the sodium hydroxide, and sometimes a little chromium. Add dilute nitric acid to the filtrate until it just turns blue litmus paper red, then add a few drops of sodium hydroxide solution to make it alkaline, boil and filter. To the filtrate add 10 c.c. of a 10 per cent. solution of lead nitrate, and then enough acetic acid to make it decidedly acid, and boil for several minutes. Filter the precipitate which contains all the vanadium as lead vanadate, and wash with hot water. Dissolve in hot dilute hydrochloric acid, evaporate nearly to dryness, add 50 c.c. of hydrochloric acid, and evaporate again, add 10 c.c. of strong sulphuric acid, and evaporate until it fumes freely.

Allow it to cool, and when cold dilute to 150 c.c., heat to a temperature of 60° or 70°, and titrate with permanganate. The iron value of the permanganate solution multiplied by 0·9157 gives the vanadium. The method of reducing vanadium by evaporating with hydrochloric acid, and then driving off the hydrochloric acid as proposed by Campagne (*Compt. Rend.*, 137, 570, 1903), gives most excellent results. The presence of small amounts of iron does not affect its accuracy, and the trouble of boiling off every trace of sulphurous acid when this reagent is used is avoided.

The two precipitates obtained from the sodium hydroxide solution contain chromium, nickel and copper, besides iron and manganese. Ignite the two filters and precipitates, and fuse with about 2 grammes of sodium carbonate and half a gramme of potassium nitrate. Treat the fused mass with water and filter. The insoluble portion contains the nickel, copper, iron, and part of the manganese, and the filtrate the chromium and the rest of the manganese. To the filtrate add ammonium nitrate in sufficient quantity to change all the sodium salts to nitrates, and evaporate to a small bulk, adding a few drops of ammonia from time to time. Dilute to about 50 c.c., boil, filter, and wash with hot water. The insoluble matter consists of manganese and any silica, alumina, &c., that may have been in the reagents. Boil the filtrate to drive off the ammonia, add sulphurous acid to reduce the chromic acid, boil off the excess and precipitate by ammonia. Filter, wash, ignite, and weigh the chromium sesquioxide which contains 68·46 per cent. of chromium.

Return the filter, containing the insoluble matter from the fusion, to the crucible in which the fusion was made, ignite, dissolve in hydrochloric acid, dilute, precipitate the copper by hydrogen sulphide, filter, and evaporate the filtrate with excess of sulphuric acid until the hydrochloric acid is expelled. Dilute, add excess of ammonia, and precipitate the nickel by electrolysis. A current of about $4\frac{1}{2}$ amperes is sufficient, and the iron and manganese present do not interfere with the accuracy of the results.

To the ethereal solution of the iron, which remains in the two separatory funnels, add water and shake. Draw off the ferric chloride containing the molybdenum, which separates from the ether, and evaporate nearly to dryness, add 10 c.c. strong sulphuric acid, and evaporate carefully until the hydrochloric acid is driven off, and the sulphuric acid fumes freely. Cool, dissolve in about 100 c.c. of water, and carefully deoxidize with ammonium bisulphite, boil off the excess of sulphurous acid, and cool the solution. Transfer the cold solution to a pressure bottle of 200 c.c. capacity and pass a current of hydrogen sulphide through it until it is saturated, close the bottle and heat it on a water bath for several hours. Allow it to cool slowly. Filter on a Gooch crucible, wash the precipitate first with water containing a little sulphuric acid, and finally with alcohol. Place the Gooch crucible containing the precipitate on a small triangle placed inside a large porcelain crucible, so that the bottom of the Gooch crucible shall not touch the bottom of the porcelain crucible. Cover the latter with a watch-glass and heat it carefully, raising the heat gradually until

there is no smell of sulphurous acid. Replace the watch-glass with a porcelain cover, and heat until the precipitate of molybdenum sulphide becomes bluish-white in colour.

Place the Gooch crucible over a lamp and heat it to faint redness, cool and weigh. Heat it again to faint redness, weigh, and repeat the operation until it ceases to lose weight. Place the crucible on the vacuum flask, and dissolve the molybdic trioxide in dilute ammonia, wash, heat, and weigh the crucible. The difference between the two weights is molybdenum trioxide, which contains 66·67 per cent of molybdenum. There always remains on the felt of the Gooch crucible a small amount of ferric oxide.

Mr. Blair found it necessary to precipitate the molybdenum sulphide from a sulphuric acid solution, as it seemed almost impossible to separate all the molybdenum sulphide in one operation from a hydro-chloric acid solution. Figures are given to show the remarkable accuracy of the method.

ANALYSIS OF QUICK-CUTTING TOOL STEEL.

PREPARATION OF THE SAMPLE.

Quick-cutting, self-hardening, or high-speed steel is, in its finished state, too hard to be drilled or turned. It must, therefore, be softened. This is conveniently done in works by embedding the sample in lime, sand, or fine ashes contained in a cast-iron or malleable-iron tube or box, ramming up tightly, placing in a smith's hearth, slowly raising the temperature, and keeping the whole till the sample has been "soaked" at a red heat for an hour or two. The sample may be allowed to cool gradually in the hearth, or may be left for some hours under hot ashes.

According to Ibbotson, the sample can be effectually softened without suffering decarbonisation by putting it in a muffle furnace, surrounded on all sides by lime or bone ash rammed tightly. The muffle is brought to a full red heat, and, after being maintained in this condition long enough for efficient "soaking," is allowed to cool slowly. When the temperature has fallen low enough to permit the insertion of the hand without discomfort, the steel may be withdrawn and can then be drilled with ease.

By the use of suitable tools, and by careful, intelligent working, fine drillings or turnings may be obtained.

Drillings or turnings from the skin of the sample should, of course, be rejected.

16

When drilling cannot conveniently be done, the steel may be broken into small pieces for analysis.

ESTIMATION OF CARBON.

Weigh off 4 grammes of the sample, which should be in the form of fine turnings or drillings, and estimate by direct combustion *at a bright red heat.* Full details are given on pp. 98 to 111.

ESTIMATION OF CHROMIUM.

GALBRAITH'S METHOD MODIFIED.[*]

Weigh off 2·4 grammes of the sample, which should be in the form of fine turnings or drillings.

Transfer the weighed sample to a 300 c.c. conical flask.

Add a mixture of 20 c.c. of concentrated sulphuric acid and 100 c.c. of water.

Heat gently, and when most of the drillings are broken up, boil rapidly down to small bulk—until solid ferrous sulphate begins to separate, or until the liquid bumps dangerously. A copious black residue remains.

Cautiously add 200 c.c. of warm water, and heat the liquid to the boiling point.

Add crystals of potassium permanganate, in very small quantities at a time, till the oxidation of the

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[*] From an account by Ibbotson in *Technics.*

iron to ferric sulphate, and chromium to chromic acid has been effected. This point is indicated when a brown precipitate is formed, which persists after boiling for a few minutes. Tungstic oxide may separate out at this period.

Add more (but not more than $\frac{1}{2}$ gramme) crystals of potassium permanganate.

Wash down any small crystals adhering to the sides of the flask.

Boil vigorously for three minutes, taking care to avoid bumping.

Transfer to a 300 c.c. graduated flask.

Cool.

Dilute to the mark, with an extra allowance of 1 c.c. for the volume of the manganese peroxide precipitate.

Filter through two dry filters into a 250 c.c. graduated flask till the filtrate reaches the mark.

The chromium and iron should now be in their highest state of oxidation.

Pour the measured portion of the filtrate into a glazed porcelain basin of about 18 cm. (about 7 inches) diameter.

Wash out the 250 c.c. graduated flask, collecting the washings in the same basin.

Add about 20 c.c. of sulphuric acid.

Get ready the articles noted on p. 154, as required for titration.

Proceed with the titration as directed on pp. 154-156.

ESTIMATION OF TUNGSTEN.

The estimation may be made as directed on pp. 213 to 225.

ESTIMATION OF MOLYBDENUM.

The estimation may be made as directed on pp. 228 to 232.

ESTIMATION OF VANADIUM.

The estimation may be made as directed on pp. 216 to 221.

ESTIMATION OF MANGANESE, PHOSPHORUS, AND SULPHUR.

"The decomposition of a high-speed steel with aqua regia is readily accomplished, and, after the removal of tungsten and silicon, the filtrate readily lends itself to the determination of sulphur, phosphorus and manganese."—Ibbotson in *Technics*.

In the solutions from weighed quantities of the sample proceed to estimate these constituents as in ordinary steel.

ANALYSIS OF ALLOYS USED IN THE MANUFACTURE OF QUICK-CUTTING STEEL.

PREPARATION OF THE SAMPLE.

Many of the alloys used in the manufacture of quick-cutting, high-speed, or self-hardening steels may be made fit for turning or drilling by the heat treatment previously described (see p. 241).

Some of the alloys may be crushed and reduced to powder in a hardened steel mortar, and the pulverising finished, where necessary, in an agate mortar. For carbon estimations the powder will be fine enough if it can readily pass through a 60-mesh sieve.

ESTIMATION OF CARBON.

One or two grammes of the sample, according to the presumed-percentage of carbon, in the form of fine turnings or of powder which has readily passed through a 60-mesh sieve, are intimately mixed with 6 grammes of copper oxide and 2 grammes of litharge, placed in a magnesite boat, or a fireclay boat with a lining of asbestos paper, and combustion proceeded with as described on pp. 98 to 111.

The aspiration of air or oxygen should be carefully controlled, and the temperature should be gradually raised to redness so as to avoid too rapid an evolution

of carbon dioxide. In the case of ferro-chrome, for instance, the purified air current should be aspirated for an hour after the highest possible temperature of the furnace has been reached. When the boat is removed after the combustion, the contents, with the exception of a few beads of metallic lead, should be black in colour and should show signs of complete fusion.

ESTIMATION OF TUNGSTEN.

The following excellent method was published by Ibbotson in *Technics :*—

"Many ferro-tungstens can be decomposed by treating them with a large excess of warm, but not boiling, hydrochloric acid, and then adding concentrated nitric acid a few drops at a time. Highly chromiferous alloys are much too refractory, however, and the following method, which is equally suitable for those which are free from chromium, gives very good results with alloys of all degrees of richness. One gramme of the alloy, through a 60-mesh sieve, is placed in a deep and capacious platinum dish provided with a lid. From 10 to 15 c.c. of hydrofluoric acid solution are then added, and the action accelerated by gently warming for no more than two minutes. The lid of the dish is then pushed aside slightly, and concentrated nitric acid added three or four drops at a time. After each addition a very vigorous action sets in, accompanied by much frothing and a copious

evolution of nitrous fumes, thus making it necessary to push the lid smartly back into position and to wait for at least a minute between each addition of the nitric acid. When the addition of the nitric acid causes no further audible action (a condition which is frequently reached after the operation of adding the three or four drops has been repeated the same number of times), the alloy has gone completely into solution with the exception of a small carbonaceous residue. The dark green solution is then allowed to digest for five minutes, and then 5 to 10 c.c. of concentrated sulphuric acid are cautiously added in drops, the lid being pushed aside slightly for the purpose.

"It is now permissible to evaporate the solution until thick fumes of sulphur trioxide escape, when the whole of the tungstic oxide will have separated. During the earlier stages of the evaporation there is a marked tendency to frothing, due apparently to the decomposition of the carbonaceous residue left unattacked by the mixture of hydrofluoric and nitric acids. It is therefore advisable to exercise considerable vigilance until this stage has been passed. The subsequent evaporation may be hastened by heating over a rose burner, but the lid of the dish should not be removed during the process.

"When copious fumes of sulphur trioxide escape, the evaporation is stopped, and, after cooling the dish, 10 c.c. of hydrochloric acid are very cautiously added, and then an equal quantity of water. The mixture is warmed for a few minutes, and the whole mass then transferred by means of the wash bottle to a capacious beaker. Except for an obstinate iridescent film on

the sides and bottom of the dish, the 'policeman' effectually removes the whole of the insoluble residue.

"The bulk of the liquid in the beaker is made up, if necessary, to about 100 c.c. with distilled water, the whole brought to boiling, and maintained in ebullition for five minutes.

"In the meantime a pulp filter (see p. 382) should be prepared, on which the tungstic oxide is collected after allowing a short time for settling. The precipitate is washed with hot water slightly acidulated with hydrochloric acid, and then transferred to the ignition dish or crucible.

"A tiny piece of ashless filter-paper soaked with one drop of ammonium hydrate will remove the film of tungstic oxide referred to above, and this can be ignited with the main precipitate.

"After ignition, the mass of tungstic oxide is invariably discoloured by contamination with ferric and chromic oxides. The amounts of these depend on many circumstances, such as, for instance, the richness of the alloy and the rate at which the preliminary 'opening out' and subsequent evaporation have been conducted. Amounts varying from 1 centigramme of ferric oxide associated with 2 milligrammes of chromic oxide, to as much as eight times each of these quantities, have been found.

"The ferric and chromic oxides are determined precisely as described under the determination of tungsten in steel " (see p. 213).

Estimation of Chromium.

Proceed as directed on pp. 147 to 151.

Estimation of Sulphur, Phosphorus, and Manganese.

The following method of " opening out," details by Horace Jervis (*Chemical News*, 5th December, 1902) and F. Ibbotson, will be found serviceable :—

To every 2·5 grammes of the sample, which should be in very fine powder or in fine drillings in a tall beaker, add 20 c.c. of 1·42 specific gravity nitric acid, and then, in small quantities at a time, add about 25 c.c. of 1·16 specific gravity hydrochloric acid.

When the action subsides, add a few crystals of potassium nitrate and apply a gentle heat with a clock glass cover in position. The mixture must not be heated to the boiling point, as this would cause bumping and would weaken the acids.

Continue to digest at a temperature near to but under the boiling point for twenty-four hours or so. A yellow residue of tungstic oxide will form (if tungsten was present). A green colour indicates imperfect decomposition.

When decomposition is complete, evaporate the liquid to low bulk, dilute with water, and separate the residue by filtering and washing. The filtrate and washings may be collected in a graduated flask, cooled, made up to the mark with water, and mixed thoroughly. Measured quantities may be withdrawn and used for the estimation of sulphur, phosphorus and manganese by the usual gravimetric methods.

ANALYSIS OF TUNGSTEN POWDER.

ESTIMATION OF CARBON.

" The amount of this element varies very much, and it often exists, even in high-class samples, in the form of charcoal. For a determination, several grammes of the alloy, unmixed with red lead, are burned in a stream of air at a red heat."—Ibbotson in *Technics.*

For details of method of estimating carbon by combustion see pp. 98 to 111.

ESTIMATION OF TUNGSTEN.

The total tungsten, metallic and oxidised, is easily determined by the method described in pp. 211 to 215. There is no correction required for the presence of chromium.

An approximate estimation of the amount of tungsten existing as sodium tungstate can be made by boiling a weighed portion of the finely-divided sample in a weak solution of sodium hydrate, filtering and washing, acidifying the filtrate with hydrochloric acid, and evaporating in a large tared platinum capsule.

ANALYSES OF IRON ORES.

DISINTEGRATION.

Many pulverised iron ores can be sufficiently disintegrated for analyses by boiling in strong hydrochloric acid solution. Ores of a more refractory nature yield only on prolonged digestion. For this purpose a tall, conical flask containing the finely-ground sample and excess of strong hydrochloric acid solution is heated nearly to the boiling point of the liquid, and set on a sand bath or hot plate arranged to keep the solution a little below the boiling point overnight. The flask should be partially closed by a small funnel.

Mr. G. W. Dean, in a recent number of the journal of the American Chemical Society,* gives results of the method of attacking iron ores by heating the weighed portion of the pulverised sample for a few minutes before treating with acid.

All iron ores yield to fusion in fusion mixture. The pulverised sample is intimately mixed with eight times its weight of fusion mixture (equal weights of pure potassium and sodium carbonates) in a capacious

* See *Chemical News*, 17th January, 1908.

platinum or nickel basin, which is set on a scorifier in a warm muffle, and kept there till the ore becomes completely fused. Fusion may, of course, be effected over a good burner or a bellows-blowpipe. When the fused mass has cooled, the basin is placed in a larger porcelain basin, and, if a platinum basin has been used, the "melt" is covered with 1·16 specific gravity hydrochloric acid, which partially dissolves and loosens the "melt." The metal basin is carefully washed, more acid is added, and heat is applied to completely dissolve the melt. If a nickel basin has been used, the melt should be dissolved in water. No solid residue should be left, except scale from the nickel basin, which should be separated by filtering.

When excess of hydrochloric acid is added to the clear solution and evaporated to dryness the silica present is rendered insoluble. On afterwards adding more hydrochloric acid, and boiling, all the constituents of the ore, except silica, will be dissolved. For details of this treatment see pp. 289 to 293.

Disintegration may be effected by fusing a weighed portion of the finely-pounded sample with about six times its weight of potassium hydrogen sulphate (potassium bisulphate, $KHSO_4$) in a large platinum basin or capsule in a muffle furnace or over a blow-pipe. Copious fumes are evolved and the ore is decomposed. When the action has ceased, and the crucible or capsule has cooled, the melt is treated with water, which dissolves all the constituents except silica. The silica may be separated on a filter and thoroughly washed, the filtrate and washings being

collected in a litre graduated flask, made up to the mark with water, and mixed well.

Measured quantities of the liquid may be withdrawn and used for estimating the percentage of any or all of the constituents except sulphur. If iron is to be estimated the measured portion should be reduced by sulphurous anhydride, excess boiled off, and the solution titrated.

Very refractory ores may be disintegrated by treating with acid under pressure. For this treatment the weighed portion of the finely-ground sample is placed, along with excess of strong hydrochloric acid, in a piece of combustion tubing which has been
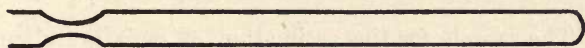
Fig. 22.—Pressure tube.

rounded and closed at one end, and drawn out to a narrow neck and funnel at the other end, as shown in sketch. The weighed sample is placed in the funnel, and washed into the tube by means of the acid solution—enough acid to half fill the tube. The narrow neck is then dried and sealed close to the shoulder. Both ends of the tube should, when softened by heat, be made as strong as possible. The tube, with its contents, is wrapped in strong iron gauze firmly wired on, and placed in a convenient vessel in which it may be heated considerably above the boiling point of the liquid. When the whole has been heated for an hour or so, it is allowed to cool gradually. The gauze is unwrapped, the tube wiped, the sealed neck is care-

fully broken, and the solution washed into a beaker if for the estimation of one constituent, or into a measuring flask if intended for more than one estimation.

The introduction of a convenient and not too costly autoclave capable of working up to two atmospheres pressure, and having an acid-proof lining, would be a boon to many analysts. In such an autoclave a weighed sample and acid in a porcelain basin might be treated.

ESTIMATION OF MOISTURE.

The sample for the estimation of moisture should be carefully selected with a due regard to the relative quantities of lumps and fines. The fines generally contain more moisture than the lumps. The sample should be quickly broken into little pieces and crushed till, on an average, much smaller than split peas.

Details of the Process.—Weigh off 25 to 50 grammes of the roughly-powdered sample in a tared platinum or porcelain capsule, and note the weight.

Place in a steam bath at 100° C., and allow to remain for about two hours.

Withdraw the capsule and contents, and allow to cool in a desiccator.

Weigh, and note the weight.

Replace the capsule and contents in the hot steam bath and maintain the temperature at 100° C.

Keep the capsule and contents there for an hour.

Withdraw them, and allow to cool in a desiccator.

Re-weigh.

If the weight is within a few milligrammes of the previous weight, calculate the percentage of moisture, but, if the weight has diminished more than a decigramme, put the capsule and contents back into the hot steam bath, and maintain the temperature at 100° C.

Keep the capsule and contents there for thirty minutes more.

Withdraw, and allow to cool in a desiccator.

Re-weigh.

Repeat the above as often as necessary—*i.e.*, until nearly constant weight is obtained.

> When experience has been gained with ores of certain classes, the necessary length of time required to dry ores of these classes will become known, so that repeated periods of drying, and reweighing, will not be necessary. A good margin of safety should, of course, be allowed.

Calculate the percentage loss.

EXAMPLE—

		Grammes.
Weight of capsule	=	24·2436
„ sample	=	25·0000
„ capsule + sample, before drying,	=	49·2436
„ „ + „ after „	=	47·6284
Loss by drying,	=	1·6152

Then, as 25 grammes were taken for the estimation, the weight lost on drying $\times \frac{100}{25}$ = percentage of moisture.

$$\frac{1 \cdot 6152 \times 100}{25} = 1 \cdot 6152 \times 4 = 6 \cdot 46 = \text{percentage}$$

of moisture in the sample.

ESTIMATION OF INSOLUBLE MATTER, ALUMINA, MANGANESE OXIDE, LIME, AND MAGNESIA IN CLAYBAND IRON-STONE.

The portion of the sample for analysis should be taken from a carefully mixed sample and ground to an impalpable powder in an agate mortar. It should then be dried in a steam bath, allowed to cool in a desiccator, and be kept in a carefully-stoppered bottle or a weighing tube.

Clayband ores may, as a rule, be sufficiently decomposed for technical purposes by boiling in hydrochloric acid. Occasionally it may be necessary to fuse the insoluble portion. For treatment of refractory ores, see pp. 251 to 254.

ESTIMATION OF INSOLUBLE MATTER.

Outline of the Process.—The weighed portion of the sample is placed in a dry basin and gently heated; it is then soaked in a little added water for a few minutes, hydrochloric acid is added and evaporated to dryness. More hydrochloric acid is measured into the basin, and, on boiling, the con-stituents of the ore, except silica and perhaps a little titanium oxide, alumina, &c., are dissolved. The soluble constituents are separated by filtration from the insoluble residue, which is dried, ignited, and

17

weighed. The ignited residue should be white or not more than faintly reddish in colour. The percentage is calculated and entered as "insoluble matter." If required, the weighed residue may be fused with fusion mixture to decompose silicate of alumina, &c., or silica may be separated from titanic oxide by means of hydrofluoric acid.

Details of the Process.—Weigh off 1 gramme of the finely-powdered sample.

Transfer the weighed portion to a 15 cm. (about 6 inches) diameter Berlin porcelain basin.

Heat gently for a few minutes over a Bunsen burner or in a muffle.

Withdraw the basin, and allow to cool.

Add about 2 c.c. of water, and stir the ore and water well.

Allow to soak for five minutes or more.

Add 20 c.c. of 1·16 specific gravity hydrochloric acid.

Evaporate to complete dryness.

Allow to cool.

Add about 15 c.c. of 1·16 specific gravity hydrochloric acid, and about 25 c.c. of hot water.

Allow to stand for a few minutes to soften the mass.

Heat to boiling point, and allow the boiling to continue for a few minutes so as to dissolve the soluble portions.

Add 20 c.c. of hot water, stir well, and filter through a 12·5 cm. Swedish filter, collecting the filtrate (and washings) in a 1,200 c.c. (about 40-oz.)

Phillip's conical beaker, or a 40-oz. globular Bohemian flask.

Wash with hot water containing a little hydrochloric acid (say 1 of acid 1·16 sp. gr., to 6 of water) about three times.

If fusion mixture has been used, as directed on pp. 251 and 289, the procedure from this point is as detailed in this and the following pages, except that particular attention must be paid to all the washings.

Wash thoroughly with hot water.
Dry the residue and filter-paper.
Ignite, cool, and weigh.
The residue, after ignition, should be pure white.
Calculate the percentage.

EXAMPLE—

		Grammes.
Weight of capsule + residue + ash =	23·4037
„ capsule . . . =	23·3133
„ residue + ash . . =	0·0904
„ ash . . . . =	0·0010
„ residue . . . =	0·0894

Then, as 1 gramme of sample was taken for the estimation, the weight of residue $\times \frac{100}{1} = $ percentage of insoluble matter.

0·0894 × 100 = 8·94 = percentage of insoluble matter in the sample of ironstone.

ESTIMATION OF ALUMINA.

Outline of the Process.—The iron in the filtrate and washings is oxidised by adding nitric acid and boiling. The acids are neutralised by addition of ammonia. Cold water and ammonium acetate are added, and the whole boiled. Iron and alumina, accompanied by the phosphoric acid present, are precipitated, and the soluble constituents are separated from the insoluble by filtering and washing. In order to free the precipitate from lime, etc., which may be held in it, and in order to obtain a precipitate of more definite composition, the receiver under the filter is changed, the precipitate is dissolved on the filter, and the solution and washings are collected in a beaker. These are neutralised, and sufficient ammonia is added to re-precipitate the iron and alumina as hydrates and phosphates. The precipitate is collected on a filter, washed, dried, ignited, and weighed. On ignition, the water is driven off, and the ignited residue, when cool, is weighed. The ferric oxide in the weighed precipitate is calculated from the percentage of iron found by titrating a weighed portion of the sample—allowance being made for the weight of phosphoric anhydride present, as ascertained by the separate estimation of this important constituent. The alumina is taken by difference. This method has been found good enough for works' practice and is regularly employed. If required, a more direct method of estimating alumina may be employed (see pp. 363 and 364).

Details of the Process.—To the filtrate and washings in the flask or conical beaker add 2 or 3 c.c. of strong nitric acid.

Boil for a few minutes so as to peroxidise the iron.

Neutralise the filtrate in the flask with ammonia liquor.

Add about 300 c.c. of cold water.

Add about 20 c.c. of ammonium acetate solution (see p. 401).

Boil.

Filter through a 20 cm., No. 598, or other thick filter, collecting the filtrate (and washings) in a 1,200 c.c. Bohemian or Jena beaker.

Wash thoroughly with hot water.

Remove the beaker containing the filtrate and washings.

Label the beaker " A," and set it to boil briskly in order to reduce the bulk of the liquid.

Dissolve the precipitate on the filter with dilute hydrochloric acid—say 1 of 1·16 specific gravity acid to 3 of water—collecting the solution (and washings) in a 1,000 c.c. Bohemian or Jena beaker.

Wash thoroughly with acid water, as above, and hot water, so as to get all the dissolved iron, &c., into the beaker.

To the contents of the beaker add a slight excess of ammonia liquor. This will precipitate the ferric oxide, alumina, and phosphoric acid present.

Boil.

Filter through an 18·5 cm. Swedish filter, collecting the filtrate (and washings) in a 1,000 c.c. Bohemian or Jena beaker.

Wash thoroughly with hot water—*i.e.*, until after all chlorides have been washed out.

Add the filtrate and washings to the liquid in the "A" beaker, taking care to avoid boiling over during the addition.

Dry the precipitate, ignite it in a red-hot muffle, and note the weight. Preserve the ignited precipitate for further use, if required. It may be dissolved and the iron in the solution estimated by titrating with standard dichrome solution.

Calculate, from the result of the estimation of the iron, the amount of ferric oxide present. Add to this the weight of phosphoric anhydride present, and deduct the combined weight of these from the total weight of the precipitate. From the difference calculate the percentage of alumina present.

Example—

		Grammes.
Weight of capsule + precipitate + ash .	=	23·1237
„ capsule	=	22·6115
„ precipitate + ash . . .	=	0·5122
„ ash	=	0·0015
„ precipitate $(Fe_2O_3 + Al_2O_3 + P_2O_5)$	$\Big\}$ =	0·5107

Note.—The precipitate of $Fe_2O_3 + Al_2O_3 + P_2O_5$ is, after weighing, dissolved in hydrochloric acid, reduced with stannous chloride, and titrated—all the precautions noted on pp. 130 to 134 being strictly observed.

The weight of iron found by calculating from the titration result is then divided by 0·7, and the result is weight of Fe_2O_3, which weight is deducted, as shown in the example.

Similarly, the weight of the P_2O_5 has to be deducted. The percentage of P_2O_5 found when estimating in a separate quantity is divided by 100, and the result (*i.e.*, the weight in 1 gramme) is deducted, as shown in the example—

		Gramme.
Weight of precipitate	=	0·5107
„ ferric oxide found from titration	=	0·4530
„ $Al_2O_3 + P_2O_5$	=	0·0577
„ P_2O_5, from separate estimation,	=	0·0211
„ $Al_2O_3 +$ ash	=	0·0366
„ ash	=	0·0010
„ Al_2O_3	=	0·0356

Then, as 1 gramme was taken for the estimation, the weight of $Al_2O_3 \times \frac{100}{1} =$ percentage of Al_2O_3.

$0·0356 \times 100 = 3·56 =$ percentage of alumina in the sample of ironstone.

ESTIMATION OF MANGANESE.

Outline of the Process.— The concentrated filtrates and washings from the previous separations are treated with bromine, ammonia is added, and, on boiling, hydrated manganese oxide is precipitated, collected on a filter, washed, dried, ignited, and weighed. From the weight obtained, the percentage is calculated.

Details of the Process.—To the contents of the beaker marked " B " add about 4 c.c. of bromine to peroxidise the manganese. Stir well while adding the bromine, and until it is all dissolved. The rubber tip of the stirring rod must be kept from contact with the drops of bromine, and should not be kept in the brominated liquid.

Allow to stand for fifteen minutes after brominating.

Cautiously add an excess of ammonia.

Stir well, and allow to settle for a few minutes.

Boil till most of the excess ammonia has been driven off. Boiling hastens the formation of hydrated manganese peroxide, and filtering is facilitated by driving off some of the excess ammonia, but the liquid must be left distinctly alkaline.

Filter through a 12·5 cm. Swedish filter, collecting the filtrate (and washings) in a 1,200 c.c. Bohemian or Jena beaker or a beaker flask. Reserve the " B " beaker (unwashed) for collecting a solution.

Wash thoroughly with hot water.

Label the beaker or beaker flask " C," and remove it.

Dissolve the precipitate on the filter with dilute hydrochloric acid—say 1 of 1·16 specific gravity acid to 3 of water—collecting the solution (and washings) in the " B " beaker, in which the hydrated manganese dioxide had been precipitated.

Add about 2 c.c. of bromine, and stir well, observing the precautions noted above.

Allow to stand for fifteen minutes after brominating.

Cautiously add an excess of ammonia.

Stir well, and allow to stand for five or ten minutes.

Boil till most of the excess ammonia has been driven off.

Filter through a 12·5 cm. Swedish filter-paper, and wash thoroughly with hot water, collecting the filtrate (and washings) in a 700 c.c. beaker labelled " D."

Place the funnel containing the filter-paper and precipitate on a dryer on a hot plate (see Fig. 4, p. 14), and allow to remain till dried.

Ignite the dried paper and precipitate in a tared platinum or porcelain crucible in a muffle furnace which is at a red heat. Allow to remain in the hot muffle for 30 minutes at least.

Allow to cool in a desiccator, weigh, and note the weight.

Correction for Co-precipitated Iron.

A small quantity of ferric oxide usually accompanies the manganese oxide, and may be easily estimated by colour, in the following manner :—

Brush the weighed substance into a 60 c.c. (about 2-oz.) Bohemian beaker.

Add about 10 c.c. of hydrochloric acid, and boil till the precipitate has dissolved.

Add about 5 c.c. of a 10 per cent. ammonium sulpho-cyanide solution.

If the mixture shows only a faint colouration, no correction is necessary.

If the mixture shows a decided colour, add about 10 c.c. of cold water, and pour the solution into a 100 c.c. stoppered graduated cylindrical measure. Rinse the beaker, and pour the rinsings into the measure. Mix well.

Measure 20 c.c. of standard iron solution ($= 0\cdot0005$ gramme of ferric oxide, see p. 408) into a corresponding stoppered graduated glass having a distinguishing mark. Add 5 c.c. of the 10 per cent. sulpho-cyanide solution, and mix well.

Compare the depth of colour of the solutions.

Dilute the more highly-coloured solution, so as to bring each to the same depth of colour.

Calculate the weight of the co-precipitated ferric oxide, thus—

Divide the weight of ferric oxide in the standard solution by its volume, and multiply the product by the volume of the solution of the oxides from the manganese estimation.

EXAMPLE.—Fe_2O_3 in standard solution $= 0\cdot0005$ gramme diluted to 25 c.c.

Solution of oxides diluted to 30 c.c.

$$\frac{0\cdot0005}{25} \times 30 = 0\cdot0006,$$

$0\cdot0006 =$ weight of co-precipitated ferric oxide.

From the previously noted weight of the ignited precipitate deduct the weight of co-precipitated ferric oxide, and from the weight of the remaining Mn_3O_4 calculate the percentage of manganous oxide (MnO) in the sample of ore.

EXAMPLE—

		Grammes.
Weight of crucible + ash + precipitate .	=	19·4387
„ crucible	=	19·4248
„ ash + precipitate . . .	=	0·0139
„ ash	=	0·0008
„ precipitate	=	0·0131
Weight of Mn_3O_4 + Fe_2O_3 . . .	=	0·0131
„ Fe_2O_3	=	0·0006
„ Mn_3O_4	=	0·0125

Trimanganic tetroxide (Mn_3O_4) contains 93·013 per cent. of manganous oxide (MnO).

$$\text{Log } 93·013 = 1·9685437.$$

Then, as 1 gramme was taken for the estimation, the weight of $Mn_3O_4 \times 93·013 =$ percentage of MnO.

$0·0125 \times 93·013 = 1·16 =$ percentage of MnO in the sample of ironstone.

Estimation of Lime.

Outline of the Process.—The filtrate from the manganese separation is boiled, and hot ammonium oxalate solution and ammonia liquor are added to cause the precipitation of the lime present as calcium oxalate. This is collected on a filter and washed, the filtrate and washings being collected in a large conical flask. The washed precipitate is dried and ignited, the resulting calcium oxide is weighed, and the percentage calculated.

Details of the Process.—Boil down the contents of beakers "C" and "D," and mix the liquids.

Add about 10 c.c. of ammonium chloride solution (see p. 402). and enough ammonia liquor to make distinctly alkaline.

Add 15 c.c. of hot ammonium oxalate [$C_2(NH_4)_2O_4$] solution (see p. 402), This will cause the precipitation of calcium oxalate (C_2CaO_4). The reaction is:—

$$CaCl_2 + C_2(NH_4)_2O_4 = C_2CaO_4 + 2(NH_4)Cl.$$

Continue the boiling for one or two minutes.

Set the beaker in a warm place to allow the precipitate to subside.

Wash the precipitate on to a 12·5 cm. Swedish filter, collecting the filtrate and washings in an 800 c.c. conical flask.

Wash thoroughly with hot water.

Dry the precipitate and filter-paper.

Place the dried precipitate and filter-paper in a tared platinum or porcelain capsule near the front of a hot muffle furnace.

After about ten minutes, remove the capsule to the hottest part of the muffle, and allow to remain there for forty minutes at least. This will cause the decomposition of the calcium oxalate; carbon monoxide and carbon dioxide will be evolved, while calcium oxide (lime) will remain.

The reaction is :—

$$CaC_2O_4 = CaO + CO_2 + CO.$$

Withdraw the capsule, and when it is just cool enough to be lifted by the hand, place it with its contents in a desiccator.

When cold, weigh.

Calculate the percentage of lime.

EXAMPLE—

		Grammes.
Weight of capsule + ash + precipitate	=	20·6738
„ capsule	=	20·6115
„ ash and precipitate	=	0·0623
„ filter ash	=	0·0008
„ precipitate (CaO)	=	0·0615

Then, as 1 gramme was taken for the estimation, the weight of CaO × $\frac{100}{1}$ = percentage of CaO.

$0·0615 × 100 = 6·15$ = percentage of lime in the sample of ironstone.

Estimation of Magnesia.

Outline of the Process.—The beaker containing the filtrate and washings from the separation of the lime is heated to about 60° C., ammonia liquor and ammonium phosphate solution are added to precipitate the magnesia as ammonium-magnesium-phosphate. The precipitate is collected on a filter, washed, dried, carefully ignited, and weighed. The percentage is then calculated.

Details of the Process.—Heat the filtrate from the separation of the lime to about 60° C.

Add about 50 c.c. of 0·88 specific gravity ammonia liquor.

Add, little by little, about 5 c.c. of 20 per cent. ammonium phosphate [$(NH_4)_2HPO_4$] solution (see p. 403).

Cork the flask, and shake it vigorously for about two minutes. (While shaking the flask, press the cork firmly to prevent its ejection.) This causes the formation of a finely crystalline precipitate of magnesium-ammonium-phosphate, $Mg(NH_4)PO_4 . 6H_2O$.

The precipitation-reaction is :—
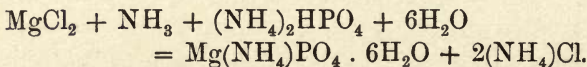
$$MgCl_2 + NH_3 + (NH_4)_2HPO_4 + 6H_2O$$
$$= Mg(NH_4)PO_4 . 6H_2O + 2(NH_4)Cl.$$

Allow the precipitate to settle for about an hour.

Decant the clear solution through a 12·5 cm. Swedish filter, and with ammonia water (1 of ammonia 0·88 specific gravity ammonia liquor to 8 of water) wash the precipitate into the filter.

Wash six times with ammonia water as above.

Test the last washings with acidulated silver nitrate (see p. 381).

Wash two or three times with the ammonia water after all the chlorides have apparently been washed out.

Dry the precipitate by placing the funnel, with filter-paper and contents, on a filter dryer (Fig. 4, p. 14), covering with paper, and allowing to dry thoroughly on the hot plate.

Place the dried filter and contents in a tared platinum or porcelain capsule, and proceed to ignite. The ignition should be cautiously begun, so as to avoid highly heating the precipitate before the organic part of the filter is burnt away. The precipitate should be white (not grey) before removing the capsule to the hottest part of the muffle, where it should remain for an hour. Unless this is done, there is danger of the precipitate so clinging to the filter-paper that it becomes impossible to burn off the paper.

During ignition the precipitate loses ammonia and water, and is converted into magnesium pyrophosphate ($Mg_2P_2O_7$), thus—

$$2Mg(NH_4)PO_4 . 6H_2O = Mg_2P_2O_7 + 2NH_3 + 7H_2O.$$

Withdraw the capsule and contents, and place in a desiccator to cool.

Weigh, and calculate.

EXAMPLE—

		Grammes.
Weight of capsule + ash + precipitate	=	21·4148
„ capsule	=	21·3135
„ ash and precipitate	=	0·1013
„ ash	=	0·0008
„ precipitate ($Mg_2P_2O_7$)	=	0·1005

The percentage of magnesia is calculated from the weight of magnesium pyrophosphate, which contains $36 \cdot 243$ per cent, of magnesia (MgO).

$$\textbf{Log } 36 \cdot 243 = 1 \cdot 5592241.$$

Then, as 1 gramme was taken for the estimation, the weight of $Mg_2P_2O_7 \times 36 \cdot 243 =$ percentage of MgO.

$0 \cdot 1005 \times 36 \cdot 243 = 3 \cdot 64 =$ percentage of magnesia in the sample of ironstone.

Estimation of Phosphoric Acid [*] (P_2O_5).

Outline of the Process.—A weighed quantity of the sample is dissolved in nitric acid, and evaporated to dryness and roasted. The dried mass is dissolved in acid and neutralised. Nitric acid, ammonium nitrate, and molybdate solutions are added to cause the precipitation of a yellow compound $[(NH_4)_3PO_4 \cdot 12MoO_3]$ containing all the phosphorus. The yellow precipitate is collected on a filter and washed, thus separating the phosphorus from the other constituents of the ore. The washed precipitate is dissolved in ammonia liquor, and the solution is neutralised. Magnesia mixture is then added to precipitate the phosphorus as magnesium-ammonium-phosphate, which is collected, washed, and dried. On ignition it is converted into magnesium pyrophosphate ($Mg_2P_2O_7$), which is weighed. From the weight of the precipitate the percentage of phosphorus in the ore is calculated.

* Correctly called phosphoric anhydride. The term "phosphoric acid" is in general use in iron and steel works.

Details of the Process.—Weigh off 3 grammes of the finely-powdered sample.

Transfer the weighed portion to a 15·5 cm. (about 6 inches) diameter Berlin porcelain basin.

Add 20 c.c. of 1·42 specific gravity nitric acid along with 20 c.c. of 1·16 specific gravity hydrochloric acid.

Evaporate to complete dryness on a hot plate (see p. 377).

Allow to cool.

Add 20 c.c. of 1·16 specific gravity hydrochloric acid.

Add about 30 c.c. of hot water.

Boil for a few minutes to dissolve the soluble constituents.

Filter through a 12·5 cm. Swedish filter, collecting the filtrate and washings in a 350 c.c. (about 12-oz.) conical flask.

Wash thoroughly with acidulated water, and then with hot water.

To the filtrate and washings add ammonia liquor until some of the iron is precipitated.

Dissolve the precipitate by adding 1·42 specific gravity nitric acid, and stirring.

Add 35 c.c. of ammonium nitrate solution (see p. 402).

Heat to 90° C. Immediately raise the thermometer about 2·5 cm. (about 1 inch) clear of the solution, and pour down the stem of the thermometer, all at once, about 150 c.c. of molybdate solution (see p. 402) into the flask. This will cause the formation of a yellow precipitate containing the phosphoric acid.

18

Withdraw the thermometer, cork the flask, and shake it vigorously for about one minute. While shaking the flask, press the fore-finger on the cork to prevent its ejection.

Pour the solution with the yellow precipitate into a 12 cm. close-texture, smooth-surface filter-paper. Rinse any remaining precipitate into the filter.

Wash the precipitate thoroughly with very dilute nitric acid—1 of 1·42 specific gravity nitric acid to 50 of water—collecting the filtrate and washings in a beaker.

Remove the beaker, and substitute for it a 500 c.c. (about 18-oz.) conical flask.

Dissolve the precipitate on the filter with dilute ammonia liquor—1 of specific gravity 0·880 ammonia liquor to 8 of water — collecting the filtrate (and washings) in the conical flask.

Wash the filter thoroughly with the dilute ammonia liquor, and afterwards with hot water, so as to dissolve all the yellow precipitate.

To the solution in the flask add enough hydrochloric acid to cause the formation of a permanent yellow precipitate.

Add about 5 c.c. more of 1·16 specific gravity hydrochloric acid. An excess is not objectionable.

Re-dissolve the precipitate with ammonia liquor.

Add to the liquid in the flask about one-sixth of its bulk of ammonia liquor of 0·88 specific gravity.

Heat the solution to about 60° C.

Add, drop by drop, about 10 c.c. of magnesia mixture (see p. 408). Agitate the flask while adding the mixture.

Cork the flask, and shake it vigorously for about two minutes. (While shaking the flask, press the cork firmly to prevent its ejection.)

This causes the formation of a finely-crystalline precipitate of magnesium - ammonium - phosphate, $Mg(NH_4)PO_4 . 6H_2O$.

The reactions may be represented thus—

(*a*) Formation of ammonium phosphate
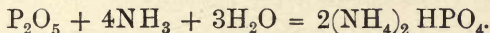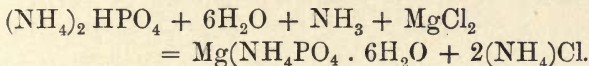
$$P_2O_5 + 4NH_3 + 3H_2O = 2(NH_4)_2 HPO_4.$$

(*b*) Precipitation of magnesium-ammonium-phosphate

$$(NH_4)_2 HPO_4 + 6H_2O + NH_3 + MgCl_2$$
$$= Mg(NH_4PO_4 . 6H_2O + 2(NH_4)Cl.$$

Allow the precipitate to settle.

Filter through a 12·5 cm. Swedish filter.

Wash about eight times with ammonia water (1 of specific gravity 0·88 ammonia liquor to 8 of water).

Test the last washings with acidulated silver nitrate solution (see p. 381).

Wash two or three times with the ammonia water after all the chlorides have apparently been washed out.

Dry the precipitate and filter.

Ignite, cool, and weigh.

The filter should be thoroughly dried, and the ignition should be cautiously begun, so as to avoid highly heating the precipitate before the organic part of the filter is burnt away. The precipitate should be white (not grey) before removing the capsule to the hottest part of the muffle, where it should remain for an hour. Unless this is done, there is danger of the

precipitate so clinging to the filter-paper that it becomes impossible to burn off the paper. During ignition the precipitate loses water, and is converted into magnesium pyrophosphate ($Mg_2P_2O_7$), thus—

$$2Mg(NH_4)PO_4 . 6H_2O = Mg_2P_2O_7 + 2NH_3 + 7H_2O.$$

Withdraw the capsule and contents, and place in a desiccator to cool.

Weigh and calculate the percentage.

EXAMPLE—

		Grammes.
Weight of capsule + ash + precipitate	=	20·7317
„ capsule . . .	=	20·6315
„ ash and precipitate . .	=	0·1002
„ filter ash . . .	=	0·0008
„ precipitate ($Mg_2P_2O_7$) .	=	0·0994

The percentage of phosphoric anhydride is calculated from the weight of magnesium pyrophosphate, which contains **63·757** per cent. of phosphoric anhydride.

When 3 grammes of sample are taken for the estimation, the factor for ascertaining the percentage is

$$\frac{63·757}{3} = 21·2523.$$

Log 21·2523 = 1·3274202.

0·0994 × 21·2523 = 2·113 ≒ 2·11 = percentage of P_2O_5 in the sample of ironstone.

Estimation of Sulphur.

Outline of the Process.—A weighed quantity of the sample is treated with pure, redistilled acid and a little potassium chlorate. The solution is evaporated to dryness, in order to render the silica insoluble and granular. The dried mass is then boiled in acid, and the insoluble residue is separated by filtration. Barium chloride is added to the clear, hot filtrate. This causes the precipitation of barium sulphate—a reaction indicated by the equation

$$K_2SO_4 + BaCl_2 = BaSO_4 + 2KCl.$$
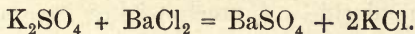
Barium sulphate is insoluble in the acid solution. It is collected on a filter, washed, dried, ignited, cooled, and weighed. The percentage of sulphur is then calculated.

Details of the Process.—Weigh off 3 grammes of the finely-powdered and dried sample.

Transfer the weighed portion to a 15·5 cm. (about 6 inches) diameter Berlin porcelain basin.

Add 30 c.c. of pure, redistilled 1·16 specific gravity hydrochloric acid, and heat gently.

When brisk action has ceased, add a few crystals of potassium chlorate.

Evaporate to complete dryness on a hot plate (see p. 377).

Allow to cool.

Add 20 c.c. of pure, redistilled 1·16 specific gravity hydrochloric acid.

Boil for a few minutes to dissolve the iron, &c.

Add about 40 c.c. of hot water, and boil for about one minute.

Filter through a 15 cm. filter, collecting the filtrate and washings in a 400 c.c. Jena or Bohemian beaker.

Wash thoroughly with a fine jet wash-bottle containing acidulated water, and then twice with water, and allow the washings to drain into the beaker. The solution and washings should not measure more than 75 c.c.

Boil.

Add, drop by drop, 5 c.c. of a 20 per cent. solution of barium chloride. A precipitate of barium sulphate will be formed if the ironstone contained sulphur.

Place a clock-glass over the beaker, and boil the contents briskly for a few minutes.

Place the beaker in a warm place, and allow the precipitate to settle — preferably overnight if the quantity is small.

Decant the liquid into a 12·5 cm. Swedish filter, collecting the filtrate and washings in a clean beaker of suitable size—say 400 c.c.

Pour about 100 c.c. of hot water and 2 c.c. of hydrochloric acid into the beaker in which the sulphate was precipitated, and shake it so as to mix the liquid and the precipitate.

Allow to settle in a warm place.

Again decant through the filter.

Pour another 100 c.c. of water into the beaker, and shake it so as to mix as before.

Drain and wash the liquid and precipitate into the filter.

Wash several times with water.

Test the last washings with acidulated silver nitrate solution.

Wash twice with water after all chlorides appear to have been washed out.

Dry the precipitate and filter-paper.

Ignite, cool, and weigh.

A blank estimation may be made on 50 c.c. of the redistilled hydrochloric acid; or the method of ascertaining the "blank" detailed on pp. 95 and 96 may be followed.

Calculate the percentage.

The percentage is calculated from the weight of barium sulphate, which contains 13·73 per cent. of sulphur.

When 3 grammes of sample are taken for the estimation, the factor for ascertaining the percentage is

$$\frac{13\cdot73}{3} = 4\cdot577.$$

Log 4·577 = 0·6605809.

EXAMPLE—

Weight of $BaSO_4$, less blank = 0·0262.

0·0262 × 4·577 = 0·1199,

and 0·12 ≑ percentage of sulphur in the sample of ironstone.

Estimation of Coaly Matter.

Outline of the Process.—A weighed quantity of the sample is treated with pure, redistilled hydrochloric acid. The solution is evaporated to dryness, in order to render the silica insoluble and granular. The dried mass is then boiled in pure hydrochloric acid, and the insoluble residue is separated by filtration. The washed residue, including the coaly matter, is washed into a tared basin, dried, and weighed. The coaly matter is burned off, the basin and contents are allowed to cool in a desiccator, and reweighed. The loss of weight by ignition is noted, allowance is made for the increase of weight due to the higher oxidation of ferrous oxide, and the percentage loss is calculated.

Details of the Process.—Weigh off 1 gramme (or more if the percentage of coaly matter is small) of the finely-pounded and dried sample.

Transfer the weighed portion to a 15·5 cm. (about 6 inches) diameter Berlin porcelain basin.

Add 20 c.c. of 1·16 specific gravity pure, redistilled hydrochloric acid.

Evaporate to complete dryness on a hot plate (see p. 377).

Allow to cool.

Add 15 c.c. of 1·16 specific gravity pure, redistilled hydrochloric acid, and about 30 c.c. of hot water.

Boil for a few minutes, to dissolve the iron, &c.

Add about 50 c.c. of hot water, and boil for about one minute.

Filter through a 15 cm. filter, collecting the filtrate and washings in a clean beaker of suitable size—say 500 c.c. capacity.

Wash three times with acidulated water (1 of 1·16 specific gravity hydrochloric acid to 6 of water).

Complete the washing with hot water.

With a fine-jet wash-bottle, wash the residue from the filter into a tared basin of about 7·6 cm. (about 3 inches) diameter.

Evaporate to complete dryness on a water bath (see p. 21).

Wipe the outside of the basin with a clean cloth which does not leave fluff, or with a piece of filter-paper.

Allow the basin and contents to cool in a desiccator.

Weigh, and note the weight.

Ignite, gently at first, in a muffle furnace until all the black matter has been burned off.

Withdraw the basin and contents, and allow to cool until the basin can be lifted by hand.

Complete the cooling in a desiccator.

Reweigh, and calculate the percentage.

EXAMPLE—

	Grammes.
Weight of basin + residue, before ignition, =	20·5006
Weight of basin + residue, after ignition, =	20·4963
Loss on ignition = coaly matter . =	0·0043

When 1 gramme of sample has been operated on, the loss of weight on ignition $\times \frac{100}{1} =$ percentage of coaly matter.

$0\cdot0043 \times 100 = 0\cdot43 =$ percentage of coaly matter in the sample of ironstone.

Estimation of Volatile Matter.

Outline of the Process.—A portion of the sample is weighed off in a tared basin. The volatile matter is driven off in a muffle furnace, and the basin, with residue, is weighed. The percentage of volatile matter is calculated from the loss of weight, after allowing for the increase in weight due to oxidation.

Details of the Process.—Weigh off 1 gramme (or more if the percentage of volatile matter is small) of the finely-pounded and dried sample.

Transfer the weighed portion to a tared platinum or porcelain basin of about 7·6 cm. (about 3 inches) diameter. Oblong porcelain trays about 5 × 3·5 cm. are also convenient for this purpose.

Heat, gently at first, in a muffle furnace, for an hour.

Withdraw the basin and contents, and allow to cool until the basin can be lifted by hand.

Complete the cooling in a desiccator.

Weigh, and note the weight.

Calculate the percentage.

EXAMPLE—

Grammes.

Weight of basin, ... = 22·6116

„ sample, ... = 1·0000

„ basin and sample, before heating, = 23·6116

„ basin and sample, after heating, = 23·3186

0·2930

During the heating the FeO is converted into Fe_2O_3. Allowance is made thus: Percentage of FeO (as per separate estimation) ÷ 900 = oxidation effect. Percentage of FeO in the ore = 38·50.

$$\frac{38·50}{900} = 0·0428,$$ weight of oxygen added to FeO during heating . . . . = 0·0428

Weight of total volatile matter . . . = 0·3358

Deduct weight of coaly matter . . . = 0·0043

Weight of other volatile matter . = 0·3315

Then, as 1 gramme was taken for the estimation, the weight × $\frac{100}{1}$ = percentage of volatile matter.

0·3315 × 100 = 33·15 = percentage of volatile matter (other than coaly matter) in the sample of ironstone.

Estimation of Carbon Dioxide.

This may be estimated by ascertaining the loss of weight due to the escape of carbon dioxide on treating a weighed portion of the sample with acid—

$$RCO_3 + 2HCl = RCl_2 + H_2O + CO_2$$
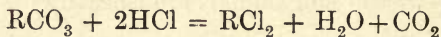
in a Schroedter-Kohn or similar apparatus.

Better results are obtained by treating a weighed sample with acid, as above, and ascertaining the increase of weight due to absorption of the carbon dioxide in a solution of caustic potash. according to the equation—

$$CO_2 + 2KHO = K_2CO_3 + H_2O$$

in a Geissler bulb.

The precautions required for carbon combustions must be observed.

The absorbing and aspirating apparatus for estimating carbon dioxide consists of—

A Berzelius gasholder (Fig. 10, p. 100).

A Dufty tower, charged as noted on pp. 99 and 100, or a large **U** tube containing caustic soda solution.

A 300 c.c. conical flask provided with (*a*) a two-hole rubber cork carrying a small separating funnel with opening at top for a rubber cork, and (*b*) an outlet tube.

An empty **U** tube for condensing vapour.

A glass drying tower (Fig. 12, p. 101) loosely packed with calcium chloride only.

A Geissler bulb (Fig. 15, p. 103) half-filled with caustic potash solution.

Another glass drying tower containing loosely-packed pieces of calcium chloride only.

These are all to be connected in the order named by means of rubber junction pieces. A tripod and Bunsen burner are also required.

The apparatus being in order :—

Weigh off 2 grammes of the finely-divided sample.

Transfer the weighed portion to the conical flask and press the moistened rubber stopper into the neck.

Through the separating funnel run, in instalments, about 10 c.c. of 1·16 specific gravity hydrochloric acid.

When action has ceased, proceed to boil gently for about five minutes.

Pass a slow current of purified and dried air through the system for seven minutes or more.

Detach and wipe the absorption bulb, place the stoppers on the ends, and allow to cool in the balance case for fifteen minutes.

Take off the stoppers, weigh the bulb with the absorbing solution, note the weight, and calculate the percentage.

EXAMPLE—

		Grammes.
Weight of charged bulb, before absorption	=	46·4075
„ „ after „	=	47·0343
Increase in weight	=	0·6268

Then, as 2 grammes were taken for the estimation, the increase in weight $\times \frac{100}{2}$ = percentage of carbon dioxide.

$0 \cdot 6268 \times 50 = 31 \cdot 34$ = percentage of carbon dioxide in the sample of ore.

For abstract of analysis and calculation of the composition of the ironstone after calcination, and also for further calculations relating to ores, see

ESTIMATION OF LESS FREQUENTLY OCCURRING ELEMENTS IN IRON ORES.

The following outline may suffice as a guide in estimating the less important elements.

ESTIMATION OF LEAD, COPPER, AND ZINC.

Separation.—Treat 5 grammes of the sample with aqua regia, take to dryness, re-dissolve in 20 c.c. of 1·16 specific gravity hydrochloric acid, and filter into a 600 c.c. flask. Neutralise with ammonia liquor, add 10 c.c. of 1·16 specific gravity hydrochloric acid and boil, reduce with 5 c.c. bisulphite solution, cool, neutralise with ammonia liquor, add 30 c.c. glacial acetic acid, and pass sulphuretted hydrogen into the *cold* solution. The precipitate may contain lead, copper, zinc, arsenic, antimony, &c. Filter, and wash with water saturated with sulphuretted hydrogen and containing some acetic acid. Dissolve the precipitate in nitric acid, add 10 c.c. of sulphuric acid, and evaporate till copious fumes appear. Cautiously add water, and collect the precipitate of lead sulphate on a small filter. Wash well, collecting the filtrate and washings in a conical flask. Pass sulphuretted hydrogen into the liquid in the flask, collect the precipitate (containing all the copper) on a filter, and wash it well. Boil off the sulphuretted hydrogen from the filtrate, oxidise by adding nitric acid and boiling, add

ammonia liquor till the liquid is distinctly alkaline, separate any precipitate by filtering and washing, collecting the filtrate containing the zinc in a suitable beaker.

Estimation of Lead. — The precipitate may be estimated from the weight of lead sulphate, or the precipitate may be dissolved in boiling ammonium acetate solution, re-precipitated as lead chromate, and the percentage of lead calculated.

Estimation of Copper.—The precipitate may be dissolved and the copper estimated by the iodine method.

Estimation of Zinc.—Zinc may be estimated in the filtrate by the sodium sulphide method or by precipitation as carbonate.

ANALYSIS OF IRON ORES, ETC., WHICH REQUIRE TREATMENT WITH FUSION MIXTURE.

Iron ores, &c., the iron of which is not soluble in boiling acid and the silicates of which are insoluble, may be decomposed by either of the two following modifications of the fusion method.

ESTIMATION OF SILICA, ALUMINA, MANGANESE OXIDE, LIME, AND MAGNESIA.

(A) *Treatment of the whole Sample with Fusion Mixture.*

Weigh off one gramme of the finely-powdered and dried sample.

Transfer the weighed portion to a capacious platinum capsule or platinum crucible.

Add 8 grammes of fusion mixture (see p. 419).

Fuse in a muffle furnace or cautiously over a good blowpipe (increasing the temperature gradually), and continue the operation until the whole of the contents have been in a state of free fusion for about 5 minutes.

Allow to cool.

Put the capsule or crucible and contents into an 18 cm. (about 7 inches) diameter Berlin porcelain basin.

Cover the "melt," *i.e.*, the result of the fusion with water.

Allow to soak for a few minutes.

Add about 5 c.c. of 1·16 specific gravity hydrochloric acid.

Wash, with a little boiling water, the dissolved portion into the basin.

Continue the treatment with small quantities of boiling water and hydrochloric acid until all the melt has been dissolved and been washed into the basin.

Set the basin and contents over a hot plate or sand bath which is heated gently.

Evaporate to complete dryness. Stirring while heating facilitates evaporation.

Allow to cool.

Add about 20 c.c. of 1·16 specific gravity hydrochloric acid.

Evaporate to dryness again.

Add about 5 c.c. of 1·16 specific gravity hydrochloric acid.

Allow to stand for about five minutes.

Add about 10 c.c. of boiling water.

Add, in small instalments, enough hydrochloric acid to dissolve the mass.

Boil.

Filter through a 15 cm. Swedish filter, collecting the filtrate (and washings) in a 1,200 c.c. (about 40-oz.) beaker or flask.

Wash several times with hot water containing one part of 1·16 specific gravity hydrochloric acid to six parts of water.

When fusion mixture has been used all the washings require to be specially well attended to. Other-

wise proceed exactly as directed from the point noted on p. 259.

The residue after treatment with fusion mixture should be returned as silica instead of insoluble matter.

(B) *Treatment of the Sample with Boiling Acid and Fusion of the Insoluble Portion.*

Weigh off 1 gramme of the finely-powdered and dried sample.

Transfer the weighed portion to a 15 cm. (about 6 inches) diameter Berlin porcelain basin.

Add about 25 c.c. of 1·16 specific gravity hydrochloric acid.

Evaporate to complete dryness.

Allow to cool.

Add about 15 c.c. of 1·16 specific gravity hydrochloric acid, and about 25 c.c. of water.

Allow to boil for a few minutes so as to dissolve the soluble portion.

Filter through a 15 cm. Swedish filter, collecting the filtrate (and washings) in a 1,200 c.c. (about 40-oz.) Bohemian beaker or flask.

Set the flask and contents aside.

Wash twice with acidulated water (say 1 part of 1·16 specific gravity hydrochloric acid to 6 parts of water).

Wash twice with hot water.

Transfer the residue and filter-paper to a capacious platinum crucible.

Dry, and then ignite the filter-paper.

Add fusion mixture (see p. 419)—about eight times the weight of the residue in the platinum dish.

Fuse cautiously in a muffle furnace or over a good blowpipe (increasing the temperature gradually), and continue the operation until the whole of the contents have been in a state of free fusion for about five minutes.

Allow to cool.

Put the platinum dish and contents into an 18 cm. (about 7 inches) diameter Berlin porcelain basin.

Cover the " melt "—*i.e.*, the result of the fusion— with hot water.

Allow to soak for a few minutes.

Add about 5 c.c. of 1·16 specific gravity hydrochloric acid.

Wash, with a little boiling water, the dissolved portion into the porcelain basin.

Continue the treatment with small quantities of boiling water and hydrochloric acid until all the melt has been dissolved and been washed into the basin.

Set the basin and contents over a hot plate or a sand bath which is heated gently.

Evaporate to complete dryness. Stirring while heating facilitates evaporation.

Allow to cool.

Add about 20 c.c. of 1·16 specific gravity hydrochloric acid.

Evaporate to dryness again.

Add about 5 c.c. of 1·16 specific gravity hydrochloric acid.

Allow to stand for about five minutes.

Add about 10 c.c. of boiling water.

Add, in small instalments, enough hydrochloric acid to dissolve the mass.

Boil.

Filter through a 15 cm. Swedish filter, collecting the filtrate (and washings) in the 40-oz. flask which contains the solution of the major portion of the ore.

Wash several times with hot water containing one part of 1·16 specific gravity hydrochloric acid to six parts of water.

When fusion mixture has been used all the washings require to be specially well attended to. Otherwise proceed exactly as directed from the point noted on p. 259.

The residue after treatment with fusion mixture should be returned as silica instead of insoluble matter.

ANALYSIS OF HEMATITE ORE.

For estimation of moisture, follow the details given on pp. 254 to 256.

For estimation of insoluble matter, alumina, manganese oxide, lime, magnesia, follow the details given on pp. 257 to 272.

For estimation of sulphur, follow the details given on pp. 277 to 279.

For estimation of phosphoric acid (P_2O_5) in hematite ore, containing more than 0·10 per cent. of phosphoric acid, follow the details given on pp. 272 to 276.

ESTIMATION OF PHOSPHORIC ACID (P_2O_5) IN THE PURER VARIETIES OF HEMATITE ORE SUITABLE FOR THE MANUFACTURE OF BESSEMER PIG IRON.

MOLYBDATE METHOD.

Outline of the Process.—The weighed sample is treated with acid, evaporated to dryness, and baked. The residue is boiled in acid and the soluble portion is separated by filtering and washing. To the filtrate, molybdate solution is added to cause the precipitation of a yellow compound containing all the phosphorus. The precipitate is collected on a filter, washed and weighed. The percentage of phosphorus is then calculated.

Details of the Process.—Weigh off 5 grammes of the finely-powdered and dried sample.

Transfer the weighed portion to a 15 cm. (about 6 inches) diameter Berlin porcelain basin.

Add 20 c.c. of 1·16 specific gravity hydrochloric acid, along with 10 c.c. of 1·42 specific gravity nitric acid.

Evaporate to dryness, and allow the basin to remain on the hot plate for five or ten minutes more. Stirring while heating facilitates evaporation.

Allow to cool.

Add 30 c.c. of 1·16 specific gravity hydrochloric acid.

Boil. Continue the boiling for a few minutes.

Add about 30 c.c. of boiling water and mix well.

Filter through a 15 cm. close-grained filter, collecting the filtrate (and washings) in a 400 c.c. Bohemian or Jena beaker.

Evaporate to small bulk—say 12 or 15 c.c.

With a fine-jet wash bottle wash the solution into a 150 c.c. (about 5-oz.) conical flask. Avoid dilution as much as possible. The solution and washings should not measure more than 30 c.c.

Add 25 c.c. of ammonium nitrate solution.

Heat to about 90° C.

Immediately raise the thermometer about 2·5 cm. (about 1 inch) clear of the solution, and pour down the stem of the thermometer, all at once, 25 c.c. of molybdate solution (see p. 402) into the flask. This will cause the formation of a yellow precipitate containing the phosphorus.

Withdraw the thermometer, cork the flask, and

shake it vigorously for about one minute. While shaking the flask, press the fore-finger on the cork to prevent its ejection.

Pour the solution with the yellow precipitate into a 9 cm. close-texture, smooth-surface filter-paper, collecting the filtrate (and washings) in a suitable beaker or conical flask. Wash any remaining precipitate on the filter.

Wash the precipitate three times with very dilute nitric acid—1 of nitric acid (1·42 specific gravity) to 50 of water.

Open out the filter-paper, and, with a fine-spout wash-bottle containing warm water, wash the precipitate on to a tared porcelain basin or a basin of platinised nickel—see note on p.   .

Evaporate on the water bath (Fig. 6, p. 21) till the precipitate is completely dried.

Wipe the outside of the basin with a clean cloth which does not leave fluff.

Allow to cool in a desiccator.

Weigh, and calculate the result.

EXAMPLE—

		Grammes.
Weight of basin + precipitate =		22·492
„ basin . . . =		22·386
„ precipitate . . =		0·106

The yellow precipitate, when thoroughly dried on a water bath, contains 1·63 per cent. of phosphorus (= 3·733 per cent. of phosphoric acid), and when 5

grammes of sample have been used for the estimation, the factor for calculation is

$$\frac{3\cdot733}{5} = 0\cdot7466.$$

Log 0·746 = $\overline{1}$·8730298.

0·106 × 0·7466 = 0·079 = percentage of phosphoric acid (P_2O_5) in the sample of ore.

If percentage of phosphorus is required the factor for 5 grammes is 0·326.

Log 0·326 = $\overline{1}$·5132176.

0·106 × 0·326 = 0·035 = percentage of phosphorus in the sample of ore.

The weighed yellow precipitate may be dissolved in ammonia liquor, magnesia mixture added to precipitate ammonium-magnesium-phosphate, the precipitate collected, washed, dried and weighed as directed on pp. 27 to 29.

ANALYSIS OF LIMESTONE.*

The volatile matter is estimated by carefully driving off all that is volatile at a steady red heat, and another sample is treated for general analysis. With one exception—magnesia—the weighed precipitates are of the same composition as the components of the limestone.

The following analysis may be made on a sample which has been finely pounded and dried. Drying, however, is not always necessary—indeed, it is unusual in iron and steel works. But, in the event of a consignment of limestone being very wet, an estimation of the moisture may be made by the method detailed on pp. 254 and 255.

Estimation of Volatile Matter.

Outline of the Process.—A portion of the sample is weighed into a tared basin, and heated at a steady red heat until all the volatile matter is driven off. After allowing to cool, the basin (with its contents) is re-weighed. The percentage loss is then calculated.

* For analysis of calcined limestone, see p. 309.

Details of the Process.—Tare a 7·6 c.m. (about 3 inches) diameter platinum or porcelain basin, and note the weight.

Weigh into it 0·8 gramme of the finely-powdered sample.

Heat gently near the front of a muffle, taking care not to permit the carrying off of solid particles.

Heat more strongly by pushing the basin and contents to the hottest part of the muffle, and allowing to remain for about an hour. By this treatment the " volatile matter " is driven off.

Withdraw the basin to the slab in front of the muffle, and, when just cool enough to permit removal by hand, place it, with its contents, in a desiccator.

When cold, weigh and calculate.

EXAMPLE—

		Grammes.
Weight of basin	=	18·3775
„ sample	=	0·8000
„ basin and sample before ignition	=	19·1775
„ „ „ after ignition	=	18·8318
Loss of weight = volatile matter . .	=	0·3457

Then, as 0·8 gramme was taken for the estimation, the loss of weight × $\frac{100}{8}$ = percentage of volatile matter.

$$\frac{0·3457 \times 100}{0·8} = 0·3457 \times 125 = 43·21 = \text{per cent.}$$

of the volatile matter in the sample of limestone.

To make sure that all volatile matter has been driven off, the basin and contents may be reheated in the hottest part of the muffle for an hour, and, after cooling in the desiccator, re-weighed.

The chief constituent of the "volatile matter" is carbon dioxide. Its percentage may be inferred from the result obtained by the following method:—

Weigh into a tared basin 5 grammes of the pounded sample.

Keep the basin and contents in a steam oven at 100° C. for about two hours.

Allow to cool in a desiccator.

The loss of weight = the water driven off; the remainder of the volatile matter may be accepted as carbon dioxide. Occasionally a little organic matter is present.

EXAMPLE—

Grammes.

Water driven off   .   .   .   = 0·024

$$0·024 \times \frac{100}{5} = 0·48,$$

and 0·48 = percentage of moisture.

Percentage of volatile matter,	.	43·21
„ water,	. . .	0·48
„ carbon dioxide,	.	42·73

When required, the percentage of carbon dioxide may be ascertained by means of a Schroedter's apparatus, or by the method detailed on pp. 284 to 286.

ESTIMATION OF INSOLUBLE MATTER.

Outline of the Process.—The weighed portion of the sample is boiled in hydrochloric acid solution, water is added, and the insoluble matter is collected on a filter, washed, dried, ignited, and weighed. From the ascertained weight the percentage is calculated.

Details of the Process.—Weigh off 1 gramme of the finely-pounded sample.

Transfer the weighed portion to a 400 c.c. beaker.

Add about 20 c.c. of warm water, and shake the beaker so as to mix the sample well with the water.

Add 10 c.c. of 1·16 specific gravity hydrochloric acid. If the limestone contains more than traces of iron, about 5 c.c. of nitric acid should also be added to facilitate separation at a subsequent stage.

Set the beaker and contents on a hot plate, and heat to boiling point.

Add about 30 c.c. of hot water.

Boil briskly.

Wash the insoluble residue into a 9 cm. Swedish filter, collecting the filtrate and washings in a 700 c.c. beaker.

Wash thoroughly with dilute hydrochloric acid—say 1 of 1·16 specific gravity acid to 10 of water—and afterwards with hot water.

Dry the residue and filter-paper.

Put the filter-paper and the residue in a tared platinum or porcelain capsule, and place in a hot muffle.

Allow to remain for half an hour.

Withdraw, and, when cool enough to just permit removal by hand, place the capsule and contents in a desiccator.

When cold, weigh.

EXAMPLE—

		Grammes.
Weight of capsule + ash + precipitate .	=	17·3933
,, capsule	=	17·3863
,, ash and precipitate . .	=	0·0070
,, filter ash	=	0·0007
,, residue	=	0·0063

Then, as 1 gramme was taken for the estimation, the weight of residue $\times \frac{100}{1}$ = percentage of residue.

0·0063 × 100 = 0·63 = percentage of insoluble residue in the sample of limestone.

The insoluble residue, as a rule, consists largely, if not entirely, of silica.   If the percentage of silica is required, it should be estimated after fusion (see method on pp. 289 to 293).

ESTIMATION OF ALUMINA.

Outline of the Process.—The filtrate from the separation of the insoluble matter is heated to boiling point, and a slight excess of ammonia liquor is added to precipitate the alumina and any ferric oxide present. Some of the excess ammonia is boiled off, the solution being left faintly alkaline. The precipitate is collected, washed, dried, ignited, and weighed. The percentage is then calculated.

Details of the Process.—To the filtrate from the insoluble matter, add 2 or 3 c.c. of 1·42 specific gravity nitric acid.

Boil.

Add a slight excess of ammonia liquor. This will cause the separation of a gelatinous precipitate of aluminium hydrate. If pure, the precipitate will be white, but if iron is present it will also be precipitated —as reddish-brown ferric hydrate.

Boil until faintly alkaline.

Immediately wash the precipitate on to a 12·5 cm. Swedish filter, collecting the filtrate and washings in a 700 c.c. beaker.

Wash several times with hot water.

Dry the precipitate and filter-paper.

Put the precipitate and filter-paper in a tared platinum or porcelain capsule, and place near the front of a muffle.

After about ten minutes, remove the capsule to the hottest part of the muffle, and allow to remain there for about thirty minutes.

Withdraw the capsule, and, when just cool enough to permit removal by hand, place it in a desiccator.

When cold, weigh.

EXAMPLE—

		Grammes.
Weight of capsule + ash + precipitate	=	17·3922
,, capsule	=	17·3863
,, ash + precipitate . .	=	0·0059
, filter ash	=	0·0008
,, precipitate (Al_2O_3) . .	=	0·0051

Then, as 1 gramme was taken for the estimation, the weight of $Al_2O_3 \times \frac{100}{1}$ = percentage of Al_2O_3.

$0·0051 \times 100 = 0·51$ = percentage of alumina in the sample of limestone.

When iron is present in appreciable amount an estimation may be made on a separate portion of the sample. The corresponding weight of ferric oxide should then be calculated and deducted from the total weight of the precipitate, the difference being taken as alumina.

Weight of Fe $\times$ 1·429 = weight of Fe_2O_3.

ESTIMATION OF LIME.

Outline of the Process.—The filtrate from the separation of the alumina is heated nearly to the boiling point. Ammonia liquor and ammonium chloride are added. A hot solution of ammonium oxalate is then added to precipitate the lime as calcium oxalate. The precipitate is collected on a filter, washed, ignited, and the resulting calcium oxide is weighed. The percentage is then calculated.

Details of the Process.—Heat the filtrate from the separation of alumina to the boiling point.

If there is reason to believe that the sample contains much magnesia, add 10 c.c. of a strong solution of ammonium chloride. This prevents the precipitation of magnesia when ammonium oxalate is added, and checks the solvent action of magnesium chloride on calcium oxalate.

Add about 10 c.c. of 0·88 specific gravity ammonia liquor.

Add 40 c.c. of hot ammonium oxalate $[C_2(NH_4)_2O_4]$ solution (see p. 402). This will cause the precipitation of calcium oxalate (C_2CaO_4). The reaction is:—

$$CaCl_2 + C_2(NH_4)_2O_4 = C_2CaO_4 + 2(NH_4)Cl.$$

Continue the boiling for about one minute.

Set the beaker in a warm place to allow the precipitate to subside.

Wash the precipitate on to a 12·5 cm. Swedish filter, collecting the filtrate and washings in a 1,000 c.c beaker.

20

Wash thoroughly with hot water.

Dry the precipitate.

Place the dried precipitate and filter-paper in a tared platinum or porcelain capsule near the front of the muffle.

After about ten minutes, remove the capsule to the hottest part of the muffle, and allow to remain there for forty minutes at least. This will cause the decomposition of the calcium oxalate: carbon monoxide and carbon dioxide will be evolved, while calcium oxide (lime) will remain.

The reaction is:—

$$CaC_2O_4 = CaO + CO_2 + CO.$$
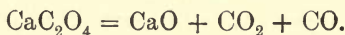
Withdraw the capsule, and, when it is just cool enough to be lifted by the hand, place it with its contents in a desiccator.

When cold, weigh.

EXAMPLE—

		Grammes.
Weight of capsule + ash + precipitate	=	18·9327
„ capsule	=	18·3773
„ ash and precipitate	=	0·5554
„ filter ash	=	0·0008
„ precipitate (CaO)	=	0·5546

Then, as 1 gramme was taken for the estimation, the weight of CaO $\times \frac{100}{1}$ = percentage of CaO.

$0·5546 \times 100 = 55·46$ = percentage of CaO in the sample of limestone.

ESTIMATION OF MAGNESIA.

Outline of the Process.—The filtrate from the separation of the lime is heated to about 60° C., and ammonium phosphate solution is added to precipitate the magnesia as ammonium-magnesium-phosphate. This is collected on a filter, washed, dried, carefully ignited, and weighed. From the weight of the resulting magnesium pyrophosphate the percentage is calculated.

Details of the Process.—To the still warm filtrate from the lime estimation add one-tenth bulk of ammonia liquor (sp. gr. 0·88).

Add about 5 c.c. of 20 per cent. ammonium phosphate $[(NH_4)_2HPO_4]$ solution (see p. 403). If the sample contained magnesia, a white precipitate of ammonium-magnesium-phosphate $[Mg(NH_4)PO_4 . 6H_2O]$ will be formed, the reaction being—

$$MgCl_2 + NH_3 + (NH_4)_2HPO_4 + 6H_2O$$
$$= Mg(NH_4)PO_4 . 6H_2O + 2(NH_4)Cl.$$
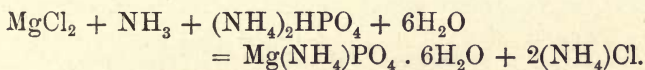
Stir briskly, and allow the precipitate to settle.

Filter through a 12·5 cm. Swedish filter.

Wash about eight times with ammonia water (1 of ammonia liquor (sp. gr. 0·88) to 8 of water),

Test the last washings with acidulated silver nitrate (see p. 381).

Wash two or three times with the ammonia water after all the chlorides have apparently been washed out.

Dry the precipitate and filter.

Ignite, cool, and weigh.

The filter should be thoroughly dried, and the ignition should be cautiously begun, so as to avoid highly heating the precipitate before the organic part of the filter is burnt away. The precipitate should be white (not grey) before removing the capsule to the hottest part of the muffle, where it should remain for an hour. Unless this is done, there is danger of the precipitate so clinging to the filter-paper that it becomes impossible to burn off the paper. During ignition, the precipitate loses water and is converted into magnesium pyrophosphate ($Mg_2P_2O_7$), thus

$$2Mg(NH_4)PO_4 . 6H_2O = Mg_2P_2O_7 + 2NH_3 + 7H_2O.$$

EXAMPLE—

		Grammes.
Weight of capsule + ash + precipitate	=	17·3946
„ capsule	=	17·3862
„ ash and precipitate . .	=	0·0084
„ filter ash	=	0·0008
„ precipitate ($Mg_2P_2O_7$) .	=	0·0076

Magnesium pyrophosphate contains 36·243 per cent. of magnesia (MgO).

$$\text{Log } 36·243 = 1·5592241.$$

Then, as 1 gramme was taken for the estimation, the weight of $Mg_2P_2O_7 \times 36·243 =$ percentage of MgO.

$0·0076 \times 36·243 = 0·275 = 0·28 =$ percentage of magnesia in the sample of limestone.

Summary of Results.—Raw limestone.

				Per cent.
Volatile matter,	.	.	.	43·21
Silica,	.	.	.	0·63
Alumina,	.	.	.	0·51
Lime,	.	.	.	55·46
Magnesia,	.	.	.	0·28
Sulphur, &c. (not estimated),	.			...
				100·09

ANALYSIS OF CALCINED LIMESTONE.

Proceed as in the analysis of limestone, but for the estimation of volatile matter use 10 grammes of the sample. For precipitating the lime, use 60 c.c. of ammonium oxalate solution (see p. 402), and for precipitating the magnesia use 4 c.c. of 20 per cent. sodium phosphate solution.

ANALYSIS OF DOLOMITE.*

Outline of the Process.—With the exception of the modifications required on account of the higher percentage of magnesia in dolomite, the method of analysis is the same as detailed for limestone in the preceding pages.

Estimation of Volatile Matter.—Proceed as directed for limestone on pp. 298 to 300, but, as the volatile matter is sometimes more difficult to drive off, continue the heating for a longer period.

Estimation of Insoluble Matter.—Proceed as directed for limestone on pp. 301 and 302.

Estimation of Alumina and Oxide of Iron.—Proceed exactly as directed on pp. 303 and 304.

Estimation of Lime.—Proceed as directed on pp. 305 and 306, except that, before precipitating the lime, add a strong solution of about 6 grammes of ammonium chloride. This prevents the precipitation of magnesia when oxalate is added, and, further, it checks the solvent action of magnesium chloride on calcium oxalate.

Estimation of Magnesia.—Proceed as directed for limestone estimation, but use 15 c.c. of the 20 per cent. ammonium phosphate solution (see p. 403).

* For analysis of calcined dolomite, see p. 312.

CALCULATION OF THE COMPOSITION OF CALCINED DOLOMITE.

Dolomite is frequently bought in the "raw" state, and is largely used in the "calcined" or "burnt" state. To find, from an analysis of raw dolomite, its composition when thoroughly burned, the following rule is useful.

Deduct the percentage of volatile matter from the total. Then divide each of the fixed components by the remainder and multiply the result by 100.

EXAMPLE.—A sample of raw dolomite had the following composition :—

Volatile matter, . . .	45·64
Silica, ...	1·85
Alumina and iron oxide, .	1·75
Lime, ...	32·24
Magnesia, ...	18·66
Sulphur, &c. (not estimated), .	...
Total, . . .	100·14

What should be the composition when calcined ?

Total, ...	100·14
Percentage of volatile matter,	45·64
„ fixed „	54·50

Now, multiply each of the fixed constituents by 100 and divide the result by 54·5.

$$1·85 \times \frac{100}{54·5} = 3·39 \text{ percentage of silica.}$$

$$1·75 \times \frac{100}{54·5} = 3·21 \qquad \text{,,} \qquad \text{alumina.}$$

$$32·24 \times \frac{100}{54·5} = 59·16 \qquad \text{,,} \qquad \text{lime.}$$

$$18·66 \times \frac{100}{54·5} = 34·24 \qquad \text{,,} \qquad \text{magnesia.}$$

$$\overline{100·00}$$

In works' practice, a little of the volatile matter remains in the calcined dolomite.

ANALYSIS OF CALCINED DOLOMITE.

Proceed as in the analysis of limestone, but, before precipitating the lime, add about 8 grammes of ammonium chloride. For precipitating the lime, use 50 c.c. of ammonium oxalate solution (see p. 402), and, for precipitating the magnesia, use 25 c.c. of the 20 per cent. sodium phosphate solution.

BLAST FURNACE SLAGS.

ESTIMATION OF INSOLUBLE MATTER, ALUMINA, MANGANESE OXIDE, LIME, AND MAGNESIA.

ESTIMATION OF INSOLUBLE MATTER.

Outline of the Process.—The weighed portion of the sample is placed in a dry beaker and gently heated on a hot plate; it is then soaked in a little added water for a few minutes, hydrochloric acid is added, and evaporated to dryness. More hydrochloric acid is measured into the beaker, and, on boiling, the soluble constituents of the slag are dissolved. These are separated by filtration from the insoluble residue, which is washed, dried, ignited, and weighed. The percentage is calculated, and entered as "insoluble matter." If required, the weighed residue may be fused with fusion mixture to decompose silicates, as directed for ore on pp. 289 to 293.

Details of the Process.—Weigh off 1 gramme of the finely-powdered sample.

Transfer the weighed portion to a 15 cm. (about 6 inches) diameter Berlin porcelain basin, or a $9 \times 7 \cdot 5$ cm. (about $3\frac{1}{2}$ by 3 inches) Bohemian or Jena beaker.

Place on a hot plate (see p. 377) and allow to remain for about ten minutes.

Allow to cool.

Add about 3 c.c. of water, and shake or stir so as to mix the sample with the water. Allow to soak for about five minutes.

Add 17 c.c. of 1·16 specific gravity pure hydrochloric acid.

Set the basin or beaker, with contents, on a hot plate, agitate from time to time so as to prevent clots, and allow to evaporate to complete dryness.

Withdraw the basin or beaker and place on a cork mat.

When the dish is not likely to crack in contact with liquid, add 15 c.c. of 1·16 specific gravity hydrochloric acid along with 15 c.c. of water. Allow to soak for about five minutes.

Boil briskly for about four minutes.

Dilute with about 25 c.c. of hot water.

Filter the solution through a 12·5 cm. Swedish filter, collecting the filtrate (and washings) in a 600 c.c. clean Bohemian or Jena beaker.

Wash the residue several times with hot water.

Dry the residue by placing the funnel with filter-paper and contents on a filter dryer (Fig. 4, p. 14), covering with paper, and allowing to dry on the hot plate.

Place the dried residue and filter-paper in a tared platinum or porcelain crucible or capsule.

Ignite in a hot muffle furnace for thirty minutes at least.

Withdraw the crucible or capsule and contents, and allow to cool in a desiccator.

Weigh quickly, and note the weight.

Calculate the percentage.

EXAMPLE—

		Grammes.
Weight of capsule + residue + ash	=	20·0742
„ capsule	=	19·7193
„ residue + ash . .	=	0·3549
„ filter ash . . .	=	0·0008
„ residue (insoluble matter)	=	0·3541

Then, as 1 gramme of the sample was taken for the estimation, the weight of residue × $\frac{100}{1}$ = percentage of insoluble matter.

0·3541 × 100 = 35·41 = percentage of insoluble matter in the sample of slag.

Estimation of Alumina.

Outline of the Process.—If the sample contained iron, nitric acid is added to the filtrate and washings from the separation of insoluble matter, and the liquid is boiled. This effects the oxidation of the iron. A slight excess of ammonia is added to cause the precipitation of aluminium hydroxide along with ferric hydroxide if the sample contained iron oxide. The reaction by which the aluminium hydroxide is precipitated may be represented by the equation—

$$Al_2Cl_6 + 6(NH_4)HO = Al_2(HO)_6 + 6(NH_4)Cl.$$
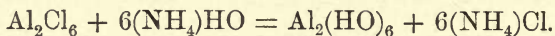
The precipitate, which will be reddish if iron is present, or white if it is absent, is collected, washed, dried, and heated strongly to drive off water.

$$Al_2(HO)_6 = Al_2O_3 + 3H_2O.$$
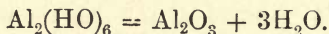
Similar reactions occur when the sample contains iron. The ignited precipitate is allowed to cool in a desiccator. It is then weighed, and iron, if present, is estimated by titration with dichrome, calculated to Fe_2O_3 and the weight deducted. If only a small quantity of Fe_2O_3 is present, it may be estimated by colour (see pp. 265 and 266). The percentage of alumina is then calculated.

Details of the Process.—Heat the filtrate and washings from the separation of insoluble matter to about 60° C. If iron is present add 2 or 3 c.c. of strong nitric acid, and boil.

Cautiously add a slight excess of ammonia liquor to neutralise the free acid and precipitate ferric and aluminium hydrates.

Boil off the excess of ammonia—that is, boil until a fresh piece of red litmus paper held in the fumes becomes only slightly changed in colour. If the solution is boiled too long, a pasty mass is left which is difficult to wash.

Immediately filter through a 12·5 cm. Swedish filter, collecting the filtrate and washings in a 1,000 c.c. clean Bohemian or Jena beaker.

Wash well with hot water. Filtering and washing of this precipitate should be done as quickly as possible.

Dry the precipitate and filter-paper, place in a tared crucible or capsule, and ignite for forty minutes or more in a hot muffle furnace. Allow to cool in a desiccator.

Weigh, and calculate the percentage.

EXAMPLE—

		Grammes.
Weight of crucible + precipitate + ash	=	22·7154
„ crucible	=	22·5543
„ precipitate + ash . .	=	0·1611
„ filter ash, . . .	=	0·0008
„ precipitate (Al_2O_3) . .	=	0·1603

Then, as 1 gramme of sample was taken for the estimation, the weight of $Al_2O_3 \times \frac{100}{1}$ = percentage of Al_2O_3.

$0·1603 \times 100 = 16·03$ = percentage of alumina in the sample of slag.

When iron is present in appreciable quantity the amount should be estimated, and the corresponding weight of ferric oxide calculated and deducted from the total weight of the precipitate, the difference being taken as alumina.

Weight of Fe × 1·429 = weight of Fe_2O_3.

If the iron in the slag is in the ferrous state, the percentage should be calculated to FeO.

$$Fe \times 1·286 = FeO.$$

Estimation of Oxide of Manganese.

Outline of the Process.—The filtrate and washings from the alumina separation are treated with bromine, ammonia is added, hydrated manganese oxide is precipitated, collected on a filter, washed, dried, ignited, and weighed.

Details of the Process.—To the filtrate and washings from the separation of the alumina add about 4 c.c. of bromine to peroxidise the manganese. Stir well while adding the bromine, and until it is all dissolved. The rubber tip of the stirring rod must be kept from contact with the drops of bromine, and should not be kept in the brominated liquid.

Allow to stand for about fifteen minutes after brominating.

Cautiously add about 20 c.c. of strong ammonia solution.

Stir well, and allow to stand for a few minutes.

Boil till most of the excess ammonia has been driven off. Boiling hastens the precipitation of hydrated manganese peroxide, and filtering is facilitated by driving off the excess ammonia—the liquid should be distinctly alkaline.

Filter through a 12·5 cm. Swedish filter-paper, collecting the filtrate (and washings) in a 1,000 c.c. clean Bohemian or Jena beaker.

Wash thoroughly with hot water.

Dry the precipitate and filter-paper, place in a tared crucible or capsule, and ignite for thirty minutes

or more in a hot muffle furnace. Allow to cool in a desiccator.

Weigh, and calculate the percentage.

EXAMPLE—

		Grammes.
Weight of capsule + precipitate + ash	=	19·7431
„ capsule	=	19·7193
„ precipitate + ash . .	=	0·0238
„ ash	=	0·0008
„ precipitate (Mn_3O_4) . .	=	0·0230

On igniting the precipitate as directed, the hydrated manganese peroxide is converted into Mn_3O_4, which contains 93·013 per cent. of manganous oxide (MnO).

$$\text{Log } 93\text{·}013 = 1\text{·}9685437.$$

Then, as 1 gramme was taken for the estimation, the weight of $Mn_3O_4 \times 93\text{·}013$ = percentage of manganous oxide.

$0\text{·}0230 \times 93\text{·}013 = 2\text{·}139$ = percentage of manganous oxide in the sample of slag.

ESTIMATION OF LIME.

Outline of the Process.—The filtrate and washings from the manganese separation are boiled, and hot ammonium oxalate solution and ammonia liquor are added to cause the precipitation of the lime present as calcium oxalate. This is collected on a filter and washed, the filtrate and washings being collected in a large conical flask. The washed precipitate is dried and ignited, the resulting calcium oxide (CaO) is weighed and the percentage calculated.

Details of the Process.—To the filtrate and washings from the previous separation add, if necessary, ammonia liquor to make the liquid distinctly alkaline.

Boil.

Add 40 c.c. of hot ammonium oxalate $[C_2(NH_4)_2O_4]$ solution (see p. 402). This will cause the precipitation of calcium oxalate (C_2CaO_4). The reaction is—

$$CaCl_2 + C_2(NH_4)_2O_4 = C_2CaO_4 + 2(NH_4)Cl.$$
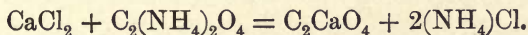
Continue the boiling for one or two minutes.

Set the beaker in a warm place to allow the precipitate to subside.

Wash the precipitate into a 12·5 cm. Swedish filter, collecting the filtrate and washings in an 800 c.c. conical flask.

Wash thoroughly with hot water.

Dry the precipitate and filter-paper.

Place the dried filter-paper containing the precipitate in a tared capsule or crucible near the front of a hot muffle furnace.

After about ten minutes remove the capsule or crucible to the hottest part of the muffle, and allow to remain there for forty minutes at least. This will cause the decomposition of the calcium oxalate; carbon monoxide and carbon dioxide will be evolved, while calcium oxide (lime) will remain.

The reaction is :—

$$C_2CaO_4 = CaO + CO + CO_2.$$
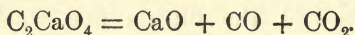
Withdraw the capsule with its contents, place in a desiccator and allow to cool.

When cold, weigh and note the weight.

Replace and allow to remain in a hot muffle furnace for twenty minutes, allow to cool in a desiccator, and reweigh. When experience has been gained with the muffle furnace, the time required for complete decomposition will be known. Some time longer should be allowed.

Calculate the percentage of lime.

EXAMPLE—

		Grammes.
Weight of crucible + precipitate + ash	=	22·9613
„ crucible	=	22·5543
„ precipitate + ash . . .	=	0·4070
„ ash	=	0·0008
„ precipitate (CaO) . . .	=	0·4062

Then, as 1 gramme was taken for the estimation, the weight of CaO $\times \frac{100}{1}$ = percentage of CaO.

$0·4062 \times 100 = 40·62$ = percentage of lime in the sample of slag.

ESTIMATION OF MAGNESIA.

Outline of the Process.—The filtrate and washings from the separation of the lime are heated to about 60° C., ammonia liquor and ammonium phosphate solution are added to precipitate the magnesia as ammonium-magnesium-phosphate. The precipitate is collected on a filter, washed, dried, carefully ignited, and weighed. The percentage is then calculated.

Details of the Process.—Heat the filtrate and washings from the previous separation to about 60° C., and add about 50 c.c. of 0·88 specific gravity ammonia liquor.

Add 6 c.c. of ammonium phosphate solution (see p. 403).

Cork the flask, and shake it vigorously for about two minutes. (While shaking the flask, press the cork firmly to prevent its ejection.) This causes the formation of a finely crystalline precipitate of magnesium-ammonium-phosphate ($Mg(NH_4)PO_4 . 6H_2O$).

Allow the precipitate to settle in a moderately warm place for about an hour.

Decant the clear solution through a 12·5 cm. Swedish filter, and with dilute ammonia liquor wash the precipitate into the filter. Collect the filtrate (and washings) in a suitable beaker.

Wash six times with dilute ammonia liquor—say 1 of 0·88 specific gravity ammonia liquor to 8 of water.

Test the last washings with acidulated silver nitrate (see p. 381).

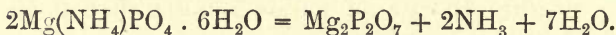Wash two or three times with the dilute ammonia

liquor after all the chlorides have apparently been washed out.

Dry the precipitate by placing the funnel, with filter-paper and contents, on a filter dryer (Fig. 4, p. 14), covering with paper, and allowing to dry thoroughly on the hot plate.

Place the dried filter and contents in a tared platinum or porcelain capsule or crucible, and proceed to ignite.

The ignition should be cautiously begun, so as to avoid highly heating the precipitate before the organic part of the filter is burnt away. The precipitate should be white (not grey) before removing the capsule to the hottest part of the muffle, where it should remain for an hour. Unless this is done, there is danger of the precipitate so clinging to the filter-paper that it becomes impossible to burn off the paper. During ignition the precipitate loses water and is converted into magnesium pyrophosphate $= (Mg_2P_2O_7)$.

$$2Mg(NH_4)PO_4 . 6H_2O = Mg_2P_2O_7 + 2NH_3 + 7H_2O.$$

Withdraw the capsule or crucible and allow to cool in a desiccator.

Weigh and calculate.

EXAMPLE—

		Grammes.
Weight of capsule + ash + precipitate	=	18·8527
„ capsule	=	18·7002
„ ash and precipitate . .	=	0·1525
„ filter ash	=	0·0008
„ precipitate $(Mg_2P_2O_7)$.	=	0·1517

The percentage of magnesia is calculated from the weight of magnesium pyrophosphate, which contains 36·243 per cent. of magnesia (MgO).

$$\text{Log } 36·243 = 1·5592241.$$

Then, as 1 gramme was taken for the estimation, the weight of $Mg_2P_2O_7 \times 36·243 = $ percentage of MgO.

$0·1517 \times 36·243 = 5·498 = $ percentage of magnesia in the sample of slag.

ANALYSIS OF PUDDLER'S CINDER, FLUE CINDER, &c.

ESTIMATION OF SILICA, ALUMINA, MANGANOUS OXIDE, LIME, AND MAGNESIA.

Proceed as directed for the analysis of clayband ironstone, pp. 257 to 271.

ESTIMATION OF SULPHUR.

Proceed as directed on pp. 277 to 279.

ESTIMATION OF PHOSPHORUS.

Weigh off 1 gramme of the finely-powdered sample. Treat with 15 c.c. of pure 1·16 specific gravity hydrochloric, and 15 c.c. of 1·42 nitric acid. Evaporate to dryness. Filter and wash well, collecting the filtrate and washings in a 250 c.c. graduated flask. When cool, add water to the mark and shake the flask vigorously to mix the liquids. Draw off 20·38 c.c. of the liquid and transfer to a 150 c.c. (about 5-oz.) conical flask. Neutralise with a few drops of ammonia liquor. Add 18 c.c. of ammonium nitrate solution (see p. 402). Heat to 90° C. Continue as directed from this point on p. 19. The weight of the dried precipitate multiplied by 20 = percentage of phosphorus in the sample of cinder. The percentage of phosphorus multiplied by 2·29 = percentage of phosphoric acid (P_2O_5).

ANALYSIS OF BASIC SLAG.

ESTIMATION OF SILICA, ALUMINA, MANGANOUS OXIDE, LIME AND MAGNESIA.

Silica may be estimated as directed on pp. 313 and 314. To the filtrate from the silica add 0·5 gramme of pure iron wire or an equivalent quantity of pure ferric chloride, so as to precipitate all the phosphoric anhydride (P_2O_5) along with aluminium and ferric hydroxides. Continue the analysis as directed on pp. 260 to 263. Deduct the weight of the ferric oxide and the phosphoric anhydride, and from the remainder calculate the percentage of **alumina**. Proceed with the estimation of **manganous oxide, lime and magnesia** as directed on pp. 264 to 272.

Ferrous and ferric oxides may be estimated as directed on pp. 139 to 146.

Sulphur may be estimated as directed on pp. 277 to 279.

ESTIMATION OF PHOSPHORIC ACID* (P_2O_5) IN BASIC SLAG.

MOLYBDATE AND MAGNESIA METHOD.

Outline of the Process.—A weighed quantity of the sample is dissolved in hydrochloric acid, evaporated to dryness, and roasted. The dried mass is

---

* Correctly called phosphoric anhydride, but the term "phosphoric acid" is in general use in iron and steel works

dissolved in acid and filtered off. Nitric acid, ammonium nitrate, and molybdate solutions are added to cause the precipitation of a yellow compound containing all the phosphorus. The yellow precipitate is collected on a filter and washed, thus separating the phosphorus from the other constituents of the basic slag. The washed precipitate is dissolved in ammonia liquor, and the solution is neutralised. Magnesia mixture is then added to precipitate the phosphorus as magnesium-ammonium-phosphate, which is collected, washed, and dried. On ignition it is converted into magnesium pyrophosphate ($Mg_2P_2O_7$), which is weighed. From the weight of the precipitate the percentage of phosphorus in the ore is calculated.

Details of the Process.—Weigh off 1 gramme of the finely-ground sample.

Transfer the weighed portion to a 12 × 10·5 cm. (about 4¾ × 4 inches) Bohemian or Jena beaker.

Add 10 c.c. of 1·16 specific gravity hydrochloric acid. If nitric acid, or impure hydrochloric acid, is used, phosphides may be oxidised and an erroneous result obtained.

Carefully evaporate to dryness on a hot plate (see note on p. 377).

Allow to stand on the hot plate for five minutes or more after evaporation to dryness.

Withdraw the beaker and place it on a cork mat.

When the beaker is not likely to crack on contact with liquid, add 10 c.c. of 1·16 specific gravity hydrochloric acid and 10 c.c. of distilled water.

Set on a hot plate and allow to remain until solution is complete and the solid residue consists of silica only.

Filter through a 15 cm. Swedish filter-paper, collecting the filtrate (and washings) in an 800 c.c. beaker.

Wash the residue on the filter four times with a solution of 1 part of 1·16 specific gravity hydrochloric acid to 4 parts of water.

Wash about five times with hot water.

Add to the filtrate and washings 30 c.c. of 0·88 specific gravity ammonia liquor.

Neutralise with pure nitric acid.

Heat to 90° C. Immediately raise the thermometer about 5 cm. (about 2 inches) clear of the solution, and pour down the stem of the thermometer, all at once, 200 c.c. of ammonium-molybdate solution (see p. 402). This will cause the formation of a yellow precipitate containing all the phosphorus.

Stir the solution vigorously to hasten precipitation.

Allow to settle at a temperature under 100° C.

Decant the clear liquor through a 15 cm. Swedish filter-paper, collecting the filtrate (and washings) in a 1,000 c.c. beaker.

Carefully rinse the precipitate into the filter, using a solution of 1 part of 1·42 specific gravity nitric acid and 20 parts of water.

Wash about seven times with the dilute nitric acid solution.

Set the beaker containing the filtrate and washings aside in a safe place for twenty-four hours, to see if a precipitate settles out. If it does, the phosphoric

acid (P_2O_5) in it must be estimated and added to the result.

Place a clean 600 c.c. conical flask under the funnel.

With a solution of 1 part of water to 2 parts of $0 \cdot 88$ specific gravity ammonia liquor dissolve the yellow precipitate, allowing the solution to collect in the conical flask.

After dissolving the precipitate, wash the filter four times with dilute ammonia liquor and three times with hot water, collecting the washings in the same conical flask.

Heat the solution and washings to about 60° C.

Add, drop by drop, to the contents of the flask 20 c.c. of magnesia mixture (see p. 408). Agitate the flask while making the additions.

Add also $0 \cdot 88$ specific gravity ammonia liquor equal to one-sixth of the bulk of the liquid in the beaker.

Cork the flask and shake it vigorously for about two minutes. (While shaking the flask press the cork firmly to prevent its ejection.) This causes the formation of a finely-crystalline precipitate of magnesium-ammonium-phosphate ($Mg(NH_4)PO_4 \cdot 6H_2O$).

Allow the precipitate to settle.

Decant the clear solution through a $12 \cdot 5$ cm. Swedish filter, collecting the filtrate (and washings) in a 1,000 c.c. beaker.

With a solution of 1 part of $0 \cdot 88$ specific gravity ammonia liquor in 8 parts of water, rinse the white precipitate into the filter.

Wash with more of the above solution, and con-

tinue the washing until, on testing, all the chlorides appear to have been washed out. Test the last washings with acidulated silver nitrite solution (see p. 381).

Wash two or three times more with the ammonia water after all the chlorides have apparently been washed out.

Dry the precipitate by placing the funnel, with filter-paper and contents, on a filter-drier (Fig. 4, p. 14) covering with paper, and allowing to dry thoroughly on the hot plate.

Place the dried filter and contents in a tared platinum or porcelain capsule and proceed to ignite. The ignition should be cautiously begun, so as to avoid highly heating the precipitate before the organic part of the filter is burnt off. The residue should be white (not grey) before removing the capsule to the hottest part of the muffle, where it should remain for an hour. Unless this is done, there is danger of the precipitate so clinging to the filter-paper that it becomes almost impossible to burn off the paper.

During ignition the precipitate loses ammonia and water, and is converted into magnesium pyrophosphate $(Mg_2P_2O_7)$, thus—

$$2Mg(NH_4)PO_4 \cdot 6H_2O = Mg_2P_2O_7 + 2NH_3 + 7H_2O.$$

Withdraw the capsule and contents to the sole in front of the muffle, and, when the capsule is just cool enough to be lifted by hand, place it in a desiccator.

When cold, weigh and calculate the percentage.

EXAMPLE—

		Grammes.
Weight of crucible + precipitate + ash	=	21·0516
„ crucible	=	20·7338
„ precipitate + ash	=	0·3178
„ filter ash	=	0·0008
„ precipitate ($Mg_2P_2O_7$)	=	0·3170

The percentage is calculated from the weight of magnesium pyrophosphate, which contains 63·757 per cent. of phosphoric anhydride.

$$\text{Log } 63\cdot757 = 1\cdot8045279.$$

Then, as 1 gramme has been taken for the estimation, the weight of $Mg_2P_2O_7 \times 63\cdot757 = $ percentage of phosphoric anhydride (P_2O_5).

$0\cdot3170 \times 63\cdot757 = 20\cdot21 = $ percentage of phosphoric acid (P_2O_5) in the sample of basic slag.

CITRATE METHOD.

Outline of the Process.—A weighed quantity of the finely-pounded sample is treated with concentrated sulphuric acid, diluted to definite bulk, and a measured portion of the resulting solution is filtered off. Magnesia mixture is added to the filtrate to cause the precipitation of all the phosphoric acid as ammonium - magnesium - phosphate. The precipitate is collected, washed, dried, ignited, and weighed. From the weight obtained the percentage of P_2O_5 is calculated.

Details of the Process.—Weigh off 5 grammes of the sample.

Transfer to a dry Bohemian flask with a mark at 250 c.c.

Add 25 c.c. of concentrated sulphuric acid.

Heat over a Bunsen flame (the flask being frequently swung round) until the fluid contents come to the boiling point.

Allow to cool.

Cautiously add water up to the mark.

Through a dry filter pour the solution and collect 50 c.c.

Measure 100 c.c. of citrate solution (see p. 404) into a 350 c.c. beaker.

Pour the 50 c.c. of filtrate into the beaker containing the 100 c.c. of citrate solution. Rinse the measures into the same beaker.

At intervals extending over ten minutes add 25 c.c. of magnesia solution, stirring vigorously all the time.

Allow the precipitate to settle.

Filter through an 11 cm. Swedish filter.

Wash well with water containing $2\frac{1}{2}$ per cent. of 0·88 ammonia liquor.

Test the final washings with acid solution of silver nitrate (see p. 381).

Wash twice with ammonia water after all chlorides appear to be washed out.

Dry the precipitate by placing the funnel, with filter-paper and contents, on a filter-drier (Fig. 4, p. 14) covering with paper, and allowing to dry thoroughly on the hot plate.

Place the dried filter and contents in a tared

platinum or porcelain capsule and proceed to ignite. The ignition should be cautiously begun, so as to avoid highly heating the precipitate before the organic part of the filter is burnt off. The residue should be white (not grey) before removing the capsule to the hottest part of the muffle, where it should remain for an hour. Unless this is done, there is danger of the precipitate so clinging to the filter-paper that it becomes almost impossible to burn off the paper.

During ignition the precipitate loses ammonia and water, and is converted into magnesium pyrophosphate ($Mg_2P_2O_7$), thus—

$$2Mg(NH_4)PO_4 . 6H_2O = Mg_2P_2O_7 + 2NH_3 + 7H_2O.$$

Withdraw the capsule and contents to the sole in front of the muffle, and, when the capsule is just cool enough to be lifted by hand, place it in a desiccator.

When cold, weigh and calculate the percentage as shown on p. 331.

ESTIMATION OF SOLUBLE PHOSPHORIC ACID (P_2O_5) IN BASIC SLAG.

In contracts for ground basic slag it is usual to stipulate that at least 80 per cent. of the slag should pass through a sieve with 100 wires each way per square inch = 10,000 mesh.

Further, it is stipulated that the price shall be fixed on the basis of the percentage of phosphoric acid (P_2O_5), of which 80 per cent. must be soluble in a 2 per cent. standard solution of citric acid.

The following particulars are given from a communication from Dr. WAGNER :—

Sampling.—The sample of slag to be analysed is sifted through a 2 mm. sieve in order to keep back the larger pieces. Any loss of the fine powder or dust is to be most carefully avoided during this operation. The sieve should, therefore, be provided with a good cover and a well-fitting receptacle. Any residue remaining in the sieve is weighed, kept back for examination, and stated as being "free from phosphoric acid" when so found.

The product of the sifting is mixed, every care being taken that no loss results from the flying off of the powder.

Estimation.— Five grammes of the sample prepared in conformity with the foregoing instructions are placed in a 500 c.c. graduated flask of the shape shown in Fig. 22, into which 5 c.c. of alcohol has previously been poured, and the flask is

1.000
C.C. m
15 °C

Fig. 23.—Graduated Flask.

filled to the mark with a 2 per cent. solution of citric acid at a temperature of 17·5° C.

The flask is then closed with a rubber stopper and placed in a rotary machine (see Fig. 23), which is then set to turn on its axis from thirty to forty times per
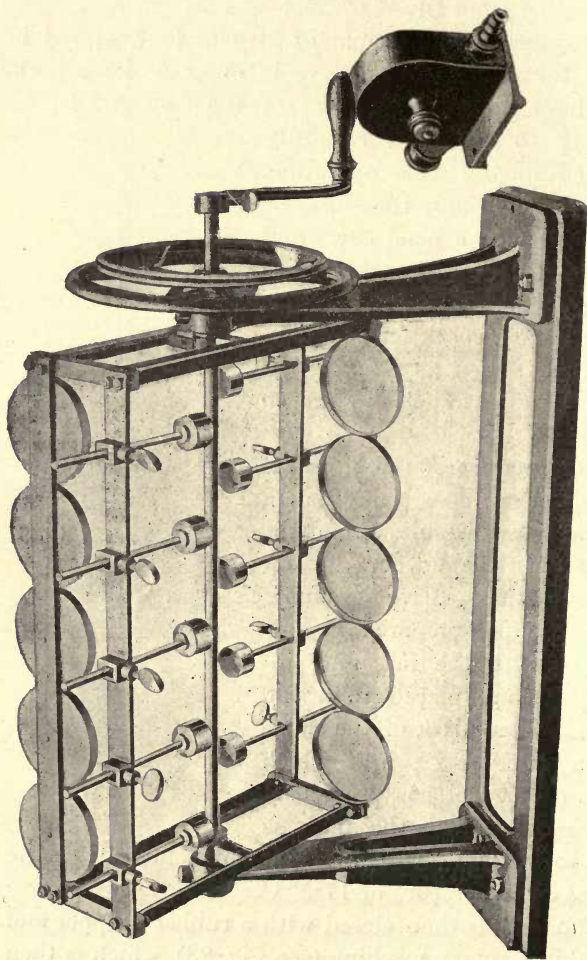
Fig. 24.—Rotary Machine.

minute. The machine is kept constantly going for thirty minutes by means of a motor at this rate. The solution is then immediately filtered.

100 c.c. of the solution is then measured into a 200 c.c. flask and 50 c.c. of citrate of magnesia (see p. 409) added. The mixture is placed on a wire gauze over a Bunsen burner and kept there, with frequent shaking, until it begins to boil. It is then quickly cooled, and an addition of 25 c.c. of 20 per cent. hydrochloric acid is added. This is allowed to stand for three-quarters of an hour, filled with water up to the mark, well shaken, and filtered. 100 c.c. of the filtrate is stirred up with 50 c.c. of 10 per cent. ammonia liquor for half an hour in a Shutzer agitating apparatus.

The further treatment of the precipitate is accomplished by the method for the estimation of total phosphoric acid (see pp. 327 to 334).

MISCELLANEOUS ESTIMATIONS.

ESTIMATION OF MANGANESE IN FERRO-MANGANESE, SPIEGEL - EISEN, SILICO-SPIEGEL, &c.

GRAVIMETRIC METHOD.

Outline of the Process.—The weighed sample is dissolved and the excess acid is carefully neutralised. A large quantity of water and a measured amount of ammonium acetate solution are added. On boiling, a precipitate consisting of basic hydrate and acetate of iron is formed, while the manganese remains in solution. These are separated by filtering and washing. To save the full amount of washing required to remove all the manganese from the precipitate it is found convenient to wash the precipitate once, dissolve and re-precipitate the iron, and again wash. Bromine is added to the mixed filtrates and washings, and, on adding ammonia, hydrated manganese oxide is precipitated. This is collected, washed, and ignited. The percentage of manganese is ascertained from the weight of the finished residue of Mn_3O_4.

Details of the Process.—Weigh off 0·5 gramme of the sample. Transfer the weighed portion to a 1,200 c.c. (about 40-oz.) globular Bohemian flask.

Add 5 c.c. of 1·42 specific gravity nitric acid, 5 c.c. of 1·16 specific gravity hydrochloric acid, and 5 c.c. of water.

Set the flask on a hot plate to hasten solution.

When the sample has dissolved add about 20 c.c. of hot water.

Boil.

Add ammonia solution till a slight permanent precipitate forms and remains in the hot liquid even after violent shaking. Much of the success of the estimation depends on the accuracy with which the neutralisation is effected.

Add about 400 c.c. of cold water.

Add 15 c.c. of ammonium acetate solution (see p. 401).

Boil briskly over the flame of a 16 mm. (about $\frac{5}{8}$-inch) Bunsen burner. If the Bohemian flask is set on a tripod, the top of which is of stout iron wire, the contents may be boiled over a large Bunsen flame, no gauze being required. When the top of the tripod has sharp edges such procedure is dangerous.

Prepare a 24 cm. (about $9\frac{1}{2}$-inch) fluted filter of No. 598 C. S. and S. or other thick filter-paper, place it in an 18 cm. (about 7-inch) funnel, saturate it with hot water, and place it in a large filter stand—see Fig. 7, p. 36. Set under it a 1,200 c.c. (about 40-oz.) Phillips' conical beaker on a dry cork mat.

Allow the *boiling* to continue for about half a minute. If the liquid nearly froths over, remove

the flask till the brisk action ceases; replace on the tripod, and allow the rapid boiling to continue. It may be necessary to remove and replace two or three times. A voluminous brown or chocolate-coloured precipitate should be formed, from which a clear yellowish-coloured liquid should drain away quickly when on the filter. The yellow colour of the liquid is due to dissolved carbide.

Immediately the boiling has finished, pour the contents of the flask on to the prepared filter, taking care not to rest the neck of the hot flask on the edge of the glass funnel, or the former may crack.

Rinse the flask with hot water and pour the rinsings on to the filter, and allow the liquid to drain off thoroughly into the conical beaker. Keep the globular flask, without more washing, for further use.

Wash once with hot water, collecting the washings in the conical beaker.

Take away the conical beaker and reduce the bulk of the liquid by boiling.

Place the 40-oz. globular Bohemian flask under the stem of the funnel.

From a wash bottle direct a stream of acidulated water (1 of 1·16 specific gravity hydrochloric acid to 2 of water) on to the precipitate so as to dissolve it.

When all the precipitate has dissolved, take away the globular flask and boil the solution.

Neutralise by adding ammonia solution till a slight permanent precipitate forms and remains in the hot liquid even after vigorous shaking.

Make up to about 400 c.c. with cold water.

Add 15 c.c. of ammonium acetate solution (see p. 401).

Boil briskly, as before.

> Prepare a 24 cm. folded filter of thick paper, as before, place it in an 18 cm. (about 7-inch) funnel, saturate it with hot water, place it in the large stand with a 600 c.c. beaker under the stem of the funnel.

Allow the *boiling* to continue for about half a minute, avoiding loss by frothing.

Immediately the boiling has finished, pour the contents of the flask into the prepared filter.

Rinse the flask twice with hot water and pour the rinsings into the filter, and allow the liquid to drain off thoroughly into the beaker.

Wash three times with hot water, collecting the washings in the beaker.

Cautiously pour the liquid from the beaker into the conical beaker containing the first filtrate, (It is advisable to collect the second filtrate in a vessel apart from the first filtrate.)

Cool the filtrate and washings.

Add about 8 c.c. of bromine to peroxidise the manganese. Stir well while adding the bromine, and until it is nearly all dissolved. The rubber tip of the stirring rod must be kept from contact with the drops of bromine, and should not be kept in the brominated liquid.

Allow to stand for about fifteen minutes after brominating.

Cautiously add enough ammonia liquor to make the solution faintly alkaline.

Stir cautiously at first, and allow to stand for a few minutes.

Boil till some of the excess ammonia has been driven off. Boiling hastens the precipitation of hydrated manganese peroxide, and filtering is facilitated by driving off most of the excess ammonia.

Filter through two 12·5 cm. Swedish filter-papers, and wash each four or five times with hot water.

Place the funnels containing the filter-papers and precipitates on dryers on a hot plate (see Fig. 4, p. 14), and allow to remain till dried.

Ignite the dried papers and precipitates in a tared platinum or porcelain crucible in a muffle furnace which is at a red heat. Allow to remain in a very hot muffle for thirty minutes at least.

Allow to cool in a desiccator, weigh, and note the weight.

Make the necessary correction for co-precipitated iron (see p. 38), and calculate the percentage of manganese from the weight of Mn_3O_4 (which contains 72·052 per cent. of manganese) obtained from the half gramme of sample.

ESTIMATION OF SILICON IN FERRO-SILICON, &c.

Ferro-silicon containing less than 18 per cent. of silicon may be decomposed by acids ; those containing more silicon require different treatment. For the lower grade materials—those made in blast-furnaces as distinguished from the products of the electric furnace — the following method gives satisfactory results :—

Weigh off about 0·8 gramme of the sample, which has been pulverised to a very fine powder in an agate mortar.

Transfer the weighed portion to a Berlin basin of about 11 cm. (about 4½ inches) diameter.

Add about 5 c.c. of water and boil gently.

Stir well with a glass rod.

Raise the rod about 2·5 cm. (about 1 inch) and pour down it about 30 c.c. of 1·16 specific gravity hydrochloric acid and 15 c.c. of 1·42 specific gravity nitric acid.

The addition of a strong solution of ferric chloride with some tartaric acid facilitates solution.

Cover the basin with a clock glass and boil briskly for fifteen minutes.

Dilute with about 30 c.c. of hot water and mix well by stirring.

Pour into a 12·5 cm. Swedish filter.

Wash with acidulated water (water, 4 parts ; 1·16 specific gravity hydrochloric acid, 1 part) several times, then two or three times with water.

Dry the residue by placing the funnel with filter paper and contents on a filter dryer (Fig. 4, p. 14), covering with paper, and allowing to dry on the hot plate.

Place the dried residue and filter-paper in a tared platinum or porcelain crucible or capsule.

In a hot muffle furnace burn off the filter-paper and ignite for about half an hour.

Withdraw the crucible or capsule and contents and allow to cool in a desiccator.

Weigh quickly and note the weight.

By the foregoing procedure a result sufficiently good for general works' purposes may be obtained. But if a more exact estimation is required, the ignited residue may be subjected to purification, as directed on p. 16, and the first filtrate may be treated in the following manner:—

Evaporate to dryness, and, when the beaker is cool enough, add 30 c.c. of 1·16 specific gravity hydro-chloric acid, and evaporate. When the beaker has again cooled sufficiently, add 20 c.c. of hydrochloric acid and 10 c.c. of water and boil briskly, filter off through a 9 cm. Swedish filter, wash the small residue with acid and water, dry, ignite, and weigh. The weight of the residue should then be added to that of the purified residue and the percentage calculated on the quantity of sample taken. For example of calculation see p. 17.

For the decomposition of higher-grade ferro-silicons —those prepared in electric furnaces—fusion of the

very finely-pounded sample in fusion mixture gives good results. 0·5 of the sample may be fused with 8 grammes of fusion mixture (see p. 419), the melt extracted and dissolved, as directed on p. 292 (except that, as a nickel capsule has been used, no acid should be used in loosening the melt from it), made up to 1 litre, and one-fourth withdrawn, evaporated, and finished, as directed on pp. 292 and 293.

Sodium peroxide may be used to decompose high-grade ferro-silicon, taking about 7 grammes for 0·5 gramme of the finely-powdered sample of 50 per cent. ferro-silicons and 8 grammes or more of peroxide for richer samples. Mix these in a nickel capsule, heat cautiously till fusion begins, raise the temperature to dull redness, and complete the fusion. Allow to cool, dissolve, and wash out with water and acidify. Evaporate to dryness, take up with acid, filter, and wash. As a precaution, evaporate the filtrate and washings, and recover any silica present. Weigh, and note the weight. After weighing, the silica may be volatilised by hydrofluoric and sulphuric acids.

0·5 gramme of finely-powdered sample may be mixed with 10 grammes of fusion mixture (see p. 419) and 2·5 grammes of powdered potassium nitrate, cautiously fused, and treated as above.

Stead's tribasic reagent (see p. 419) may be used to decompose rich ferro-silicons, and potassium bisulphate has also been recommended.

VOLUMETRIC ESTIMATION OF MANGANESE.

BASED ON PATTINSON'S METHOD.

ESTIMATION OF MANGANESE IN ORE.

Outline of the Process.—A weighed quantity of the finely-pounded sample is dissolved in acid, or, if necessary, is fused, and the melt is dissolved. By the action of bleaching powder the iron in the ore is converted into the ferric state, and the manganese is also converted to one of its highest states of combination.

A known amount (which must be in excess) of ferrous salt or solution is then added. Some of this is converted into the ferric condition by the action of the manganese compound in the solution.

For convenience, the reaction may be represented thus:—

$$MnO_2 + 2FeO = Fe_2O_3 + MnO.$$
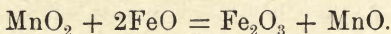
The excess of ferrous oxide is ascertained by titrating with standard dichrome solution, and from the difference (that is, the amount oxidised by the manganese salt), the percentage of manganese in the ore is ascertained

Details of the Process.—Weigh off 0·5 gramme of the finely-pounded sample.

Transfer the weighed portion to a 12·5 × 10 cm. (about 5 × 4 inches) beaker.

Add 10 c.c. of 1·16 specific gravity hydrochloric acid.

Boil till all the manganese oxide is dissolved, and much of the excess acid has been driven off.

If the ore is not readily soluble in acid, decompose by fusion in the following manner :—

Weigh off 6 grammes of fusion mixture (see p. 419).

Spread the weighed portion in a 7·5 cm. (about 3 inches) diameter nickel or platinum capsule.

Weigh off 0·5 gramme of the finely-pounded sample of ore.

Mix the ore carefully with the fusion mixture

Fuse over a blowpipe or in a muffle furnace.

When cool, place the capsule in a glazed porcelain basin of 18 cm. (about 7 inches) diameter.

Pour water into the capsule and allow the melt to loosen or dissolve.

Pour the solution into a 12·5 × 10 cm. (about 5 × 4 inches) beaker.

Rinse the solution in the porcelain basin into the beaker.

Rinse the remainder of the melt from the capsule, using a rubber end to detach any portion which sticks. By boiling a little water in the capsule any still-clinging melt may be loosened.

Add hydrochloric acid to the liquid in the beaker—more than enough to neutralise, and to dissolve the soluble matter.

Almost cover the beaker with a clock-glass.

Evaporate on a hot plate to small bulk, and to remove excess of acid.

Rinse the cover and the inside of the beaker with warm water.

By whichever method the sample has been attracted :—

Add to the solution in the beaker solid pure precipitated calcium carbonate until a slight permanent precipitate forms.

Redissolve the precipitate by adding a small quantity of hydrochloric acid—leaving the solution faintly acid.

Add 5 c.c. of 10 per cent. zinc chloride solution (see p. 418).

Add about 300 c.c. of boiling water, and about 70 c.c. of bleaching powder solution (see p. 404), to which just enough hydrochloric acid has been added to give it a faint permanent greenish-yellow colour after gentle agitation. The object of this addition of acid is to prevent a local precipitation of manganese in a lower state of oxidation than MnO_2. The solution should remain clear on the addition of the bleaching powder.

Stir the liquid, and gradually add about 5 grammes of pure calcium carbonate diffused in about 25 c.c. of hot water. After the first evolution of carbonic acid (during which time the cover is kept on the beaker) has ceased, the precipitate is stirred to make it collect together, about 2 c.c. of methylated spirits are added, and it is again stirred. This should cause the formation of a quickly-settling precipitate containing all the manganese as dioxide.

Collect the precipitate in an 18 cm. plaited filter, collect the filtrate (and washings) in a beaker of convenient size.

Wash several times with cold water, and, when the greater part of the chlorine has been removed, with warm water (about 70° C.). Continue the washing

until on testing with acidulated silver nitrate solution (see p. 381) no chlorine appears to be present. Wash three times more with warm water.

Place the precipitate and filter-paper in an 18 cm. (about 7 inches) diameter porcelain basin.

Measure about 20 c.c. of water and about 10 c.c. of 1·84 specific gravity sulphuric acid into the basin.

Stir, so as to mix the water and acid.

Weigh off, accurately, about 5 grammes of Mohr's salt (see p. 122), and note the weight taken.

Put the weighed portion in the basin, and stir until the salt is dissolved.

Adjust the solution in the burette to zero.

Titrate, as directed on pp. 130 to 133.

Note the quantity of solution required to complete the reaction.

Calculate as in the following example :—

EXAMPLE—

		Grammes.
Weight of ore taken	=	0·5026
,, of Mohr's salt taken . .	=	5·1324

$$\text{Iron in Mohr's salt taken} = \frac{5 \cdot 1324 \times 14 \cdot 26}{100} = 0 \cdot 73188$$

Dichrome solution required = 23·2 c.c., of which each c.c. = 0·0102 gramme of iron.

$$23 \cdot 2 \times 0 \cdot 0102 = 0 \cdot 23664.$$

Iron in Mohr's salt	=	0·73118
,, represented by the standard dichrome used	=	0·23664
,, oxidised by MnO_2 in the sample of ore	=	0·49454

The equation formerly given shows that 111·8 parts, by weight of iron, are equivalent to 55 parts, by weight of manganese.

$$\frac{0\cdot49454 \times 55 \times 100}{111\cdot8 \times 0\cdot5026} = \frac{0\cdot49454}{0\cdot5026} \times 49\cdot19 = 48\cdot40$$

= percentage of manganese in the sample of ore.

RAPID ESTIMATION OF LIME IN LIMESTONE, DOLOMITE, OR SLAG.

ULK'S (VOLUMETRIC) METHOD.

Outline of the Process.—The weighed portion of the finely-pounded sample is treated with acid to dissolve the soluble constituents, and these are separated by filtration and washing. When experience of this rapid method has been gained, it may not be necessary to separate the insoluble matter. The filtrate and washings are neutralised, and hot ammonium oxalate solution is added to precipitate the lime. The precipitate is collected, washed, and dissolved in excess of sulphuric acid. By this means the calcium oxalate is decomposed, calcium sulphate and oxalic acid being formed—

$$C_2CaO_4 + H_2SO_4 = CaSO_4 + C_2H_2O_4.$$
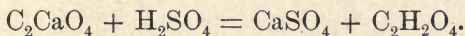
The amount of oxalic acid present is measured by the reduction, and decolourising, of standard potassium permanganate solution.

A decinormal solution of potassium permanganate contains 3·163 grammes per litre, and 1 c.c. of such a solution corresponds to 0·0063 gramme of crystallised oxalic acid ($C_2H_2O_4 . 2H_2O$), or 0·0028 gramme of lime.

A solution containing 11·2967 grammes of pure potassium permanganate per litre corresponds to 0·01 gramme of lime per c.c.

A standard solution of this strength may be made as directed on p. 121, and standardised either with standard solution of oxalic acid, or with Mohr's salt as directed on pp. 123 and 125.

A permanganate solution which has been prepared for the estimation of iron and standardised may be used, the factor for Fe × 0·50089 corresponding to CaO, or 0·01 gramme of Fe corresponding approximately to 0·005 gramme of lime when titrated with standard potassium permanganate solution. As 0·5 gramme of sample is usually taken for the estimation of CaO, the Fe factor will, of course, approximately correspond without correction.

In standardising with oxalic acid the directions given in *Sutton's Volumetric Analysis* should be followed.

The measured solution is "brought into a flask with dilute sulphuric acid, as in the case of the iron salt, and considerably diluted with water, then warmed to about 58° C., and the permanganate measured from a burette. The colour disappears slowly at first but afterwards more rapidly, becoming at first brown, then yellow, and so on to colourless. More care must be exercised in this case than in the titration with iron, as the action is less decisive and rapid, nevertheless, it is as reliable with care and attention."

Details of the Process.—Weigh off 0·5 gramme of the finely-pounded sample.

Transfer the weighed portion to a 500 c.c. beaker.

Add 6 c.c. of 1·42 specific gravity nitric acid along with 30 c.c. of hot water.

Boil till all the soluble constituents are dissolved.

Add about 150 c.c. of water and a drop or two of strong sulphuric acid.

Heat to boiling point and cautiously add ammonia liquor (stirring constantly during the addition) till the solution is just neutral.

Add 70 c.c. of hot ammonium oxalate solution (see p. 402). This will cause the precipitation of calcium oxalate (CaC_2O_4) with perhaps a little iron.

Cover the beaker with a clock-glass and allow boiling to continue for a few minutes.

Allow the residue and precipitate to settle.

Collect on a 12·5 c.m. Swedish filter, collecting the filtrate (and washings) in a convenient sized beaker.

Wash two or three times with hot water and once with ammonia liquor. Wash twice more with hot water.

Wash, with warm water, the residue and precipitate from the filter into an 18 c.m. (about 7 inches) diameter porcelain basin.

Stir so as to thoroughly mix and make a cream of the washed off residue and precipitate with the water.

Add about 100 c.c. of water.

Cautiously add, with constant stirring, 25 c.c. of 1·84 specific gravity sulphuric acid.

Instead of the 100 c.c. of water and 25 c.c. of acid, 125 c.c. of sulphuric acid for lime estimation (see p. 417) may be used.

Stir the whole so as to dissolve the calcium oxalate.

Titrate with standard potassium permanganate solution, keeping the solution at a temperature of about 60° C. while titrating.

Calculate the percentage.

EXAMPLE.—0·503 gramme of the sample taken for the estimation. This required 26·83 c.c. of standardised potassium permanganate solution, each c.c. of which was equal to 0·0099 gramme of lime.

$$\frac{26 \cdot 83 \times 0 \cdot 0099 \times 100}{0 \cdot 503} = 52 \cdot 805 = \text{percentage of}$$

lime in the sample.

ESTIMATION OF TITANIUM IN IRON ORES.

Weigh off 1 or 2 grammes of the finely-pounded sample.

Transfer the weighed portion, along with 1 gramme of sodium ammonium phosphate, to a 15 cm. (about 6 inches) diameter Berlin porcelain basin.

Add 30 c.c. of 1·16 specific gravity hydrochloric acid.

Evaporate to dryness.

Weigh the residue and grind it in an agate mortar with 10 times its weight of sodium carbonate or fusion mixture.

Transfer to a nickel basin and fuse over a blow-pipe or a Mecker burner.

Allow to cool.

Boil with distilled water.

Collect the residue on a filter and wash.

With very little water wash the residue into a beaker.

Add 5 c.c. of 1·16 specific gravity hydrochloric acid, 2 c.c. of 1·51 specific gravity sulphuric acid, and 8 c.c. of water.

Evaporate until all the hydrochloric acid is expelled and white fumes of SO_3 come off.

Cool, dilute, boil, filter, and wash.

Dilute to about 150 c.c.

Add ammonia solution until a slight precipitate forms, just re-dissolve this in hydrochloric acid, and reduce with sulphurous anhydride solution.

As soon as the solution is colourless add 30 c.c. of 1·045 specific gravity acetic acid and 10 grammes of sodium acetate.

Boil.

Titanium oxide (TiO_2) will separate, but may be impure. If, however, it is re-dissolved and re-precipitated, the TiO_2 will be pure, and should be white.

Collect the precipitate on a 12·5 cm. Swedish filter and wash.

Dry the washed precipitate, ignite, allow to cool, weigh, and calculate the percentage.

The pure oxide contains 60·05 per cent. of titanium.

$$Log\ 60·05 = 1·7785130.$$

ESTIMATION OF PHOSPHORUS IN PIG IRON CONTAINING TITANIUM.

Dissolve the weighed portion—say 2 grammes—in acid.

Evaporate to dryness, re-dissolve, filter, and wash.

Preserve the filtrate and washings.

Dry and ignite the residue, so as to drive off the graphite.

Fuse the ignited residue (which contains oxides of phosphorus, titanium, and iron) with sodium carbonate.

Extract the melt with hot water, filter, and wash.

Acidify the clear filtrate and washings with hydrochloric acid.

Add pure ferric chloride solution — more than sufficient to combine with the phosphoric anhydride present.

Cautiously add dilute ammonia liquor or solution of ammonium carbonate ; ferric phosphate, which is white, will first be precipitated, and, on continuing to add ammonia solution or ammonium carbonate, the precipitate will become brown if enough ferric chloride is present.

Boil.

Collect the precipitate on a Swedish filter and wash with warm water.

Take away the beaker containing the filtrate and washings.

Place a clean beaker under the funnel and dissolve the precipitate on the filter by means of hydrochloric acid.

Wash the filter-paper with hot water, collecting the washings in the same beaker.

Evaporate the solution and washings to dryness, treat the dried residue with hydrochloric acid, and separate the insoluble residue on a filter.

Wash the residue, collecting the filtrate and washings in the beaker containing the first filtrate and washings.

Add 35 c.c. of ammonium nitrate solution and proceed with the estimation of phosphorus as directed on pp. 70 to 73.

VALUATION OF FLUOR SPAR.

The following outline of the method used in one of the leading English steel works was supplied by one of my students :—

ESTIMATION OF CARBON DIOXIDE.

Two grammes of the finely-powdered sample (dried at 110° C.) are ignited at a full red heat in a muffle furnace.

The loss of weight × 50 = percentage of carbon dioxide.

ESTIMATION OF SILICA.

Two grammes of the powdered sample (dried at 110° C.) are treated with a little pure hydrofluoric acid in a tared platinum crucible, evaporated to dryness, in front of the muffle, and, finally, ignited.

The loss in weight = $SiO_2 + \frac{1}{2}CO_2$, since the silica forms silicon tetrafluoride (SiF_4), which is volatilised, and the calcium carbonate ($CaCO_3$) present is converted into calcium fluoride (CaF_2)—

$$\underbrace{CaCO_3}_{100} + 2HF = \underbrace{CaF_2}_{78} + CO_2 + H_2O.$$
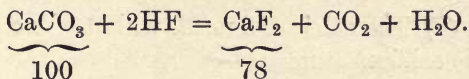
Whence $100 - 78 = 22$, or half the molecular weight of CO_2.

Therefore, subtract half the loss in weight in the carbon dioxide estimation from the loss in weight in this estimation. Then, as 2 grammes were taken for the estimation, the difference × 50 = percentage of silica.

EXAMPLE—

Loss on ignition of 2 grammes = 0·042 gramme.
Loss on treatment of 2 grammes with hydrofluoric
    acid = 0·124 gramme.

$$\tfrac{1}{2}CO_2 = 0·021.$$
$$0·124 - 0·021 = 0·103.$$

0·103 × 50 = 5·15 = percentage of silica.

ESTIMATION OF CALCIUM FLUORIDE.

Two grammes of the finely-powdered sample (dried at 110° C.) are treated with concentrated sulphuric acid in a tared platinum crucible. The results of this treatment will be—

(a) The calcium carbonate will be converted into calcium sulphate—

$$\underset{100}{CaCO_3} + H_2SO_4 = \underset{136}{CaSO_4} + CO_2 + H_2O.$$
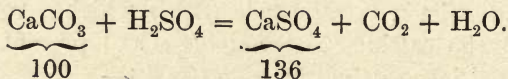
(b) The calcium fluoride will also be converted into calcium sulphate—

$$\underset{78}{CaF_2} + H_2SO_4 = \underset{136}{CaSO_4} + 2HF.$$
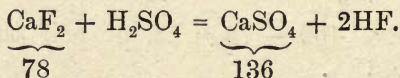
(c) The silica will combine with fluorine and will be volatilised as silicon tetrafluoride.

The crucible is taken to dryness in front of the muffle and afterwards strongly ignited. There will be a gain in weight. Add this gain in weight to the weight of silica found. Multiply the weight of carbon dioxide obtained from 2 grammes by 0·818, in order to find the increase in weight due to calcium sulphate obtained from the calcium carbonate.

EXAMPLE—

	Grammes.
Gain in weight on treating 2 grammes with sulphuric acid	= 1·1615
Add weight of silica in 2 grammes . .	= 0·1030
	1·2645

Subtract gain in weight due to conversion of calcium carbonate into calcium sulphate = weight of carbon dioxide × 0·818 = 0·040 × 0·818 . . .	= 0·0327
	1·2318

1·2318 grammes = increase in weight due to the conversion of the calcium fluoride, in 2 grammes, to calcium sulphate.

1·2318 × 67·25 = 82·64 = percentage of calcium fluoride in the sample of fluor spar.

OUTLINE OF METHODS FOR THE ESTIMATION OF ONE CONSTITUENT ONLY OF IRON ORE, SLAG, LIMESTONE, DOLOMITE, &c.

ESTIMATION OF SILICA.

Proceed exactly as directed on pp. 257 to 259 for ores; pp. 301 to 302 for limestone or dolomite; or pp. 313 to 315 for slags. Or fuse with potassium bisulphate (see p. 16), extract with water and acid, collect the insoluble residue on a filter, wash well, dry, ignite, and weigh the silica. Calculate the percentage.

ESTIMATION OF ALUMINA.

(A) In blast-furnace slags which are free, or nearly free, from iron.

Weigh off 1 gramme of the finely-powdered sample, treat with acid, and separate the silica as directed in the paragraph above. To the filtrate and washings add a slight excess of ammonia solution, and boil till only faintly alkaline. Filter off at once and wash quickly several times with hot water, collecting the filtrate and washings in a suitable beaker. Remove the beaker and place a clean 600 c.c. beaker under the funnel. With warm water, acidulated with hydrochloric acid, dissolve the washed precipitate.

Wash twice after all the dissolved precipitate appears to have been washed into the beaker. To the warm filtrate and washings add ammonia solution till just neutral. Dilute with hot water to about 500 c.c. Boil. Immediately collect the precipitate on a filter and wash quickly. Dry and ignite the precipitate. Weigh and calculate the percentage.

(B) **In iron ores, or in slags or cinders containing much iron.**

Weigh off 1 gramme of the finely-divided sample and treat with pure hydrochloric acid in a conical flask carrying a delivery tube and water seal (see Fig. 19, p. 140). Quickly filter and wash the insoluble residue, collecting the filtrate and washings in a conical flask. If thought desirable, pass sulphurous anhydride into the liquid to reduce all the iron to the ferrous state. Fit a cork carrying a delivery tube leading to a water seal and boil off the excess sulphurous anhydride. Add to the hot solution a slight excess of ammonia liquor to precipitate the alumina as phosphate and hydrate. Boil for a minute. Quickly collect on a filter and wash with warm water.

If there is reason to believe that lime or other constituent is held in the gelatinous precipitate, dissolve the precipitate, neutralise, re-precipitate with ammonia solution, and wash. Change the beaker under the filter. Re-dissolve, make just alkaline, and add ammonium phosphate solution. Collect the precipitate and wash. Dry, ignite, and weigh the precipitate.

If iron is present, dissolve the weighed precipitate,

estimate the iron, and deduct the weight of ferric phosphate ($FePO_4$).

If there is reason to believe that the insoluble matter contained alumina, it should be fused and the alumina estimated.

Make any necessary subtraction or addition and calculate the percentage.

ESTIMATION OF MANGANESE OXIDE.

Manganese may, in many instances, be conveniently estimated by the Pattinson process (see pp. 346 to 350) or by the following gravimetric method:—

In a 1,200 c.c. (about 40 ozs.) Bohemian flask treat the weighed portion of the finely-powdered sample with acid so as to dissolve all the soluble constituents and oxidise any ferrous iron which may be present. Cautiously add ammonia solution till a faint persistent precipitate is formed. Add about 400 c.c. of cold water. Add 30 c.c. of ammonium acetate solution. Boil briskly and filter through a large thick filter. Wash several times with warm water. The filtering and washing should be quickly done. If the precipitate is bulky, change the receiver and dissolve the precipitate. To the solution add ammonia solution to re-precipitate the iron and alumina. Collect the precipitate on a filter and quickly wash it with warm water. Brominate the filtrate (or filtrates) and washings (ores require a plentiful addition of bromine) and allow to stand for fifteen minutes or more.

Cautiously add ammonia liquor in excess and allow
to stand for fifteen minutes. Boil off some of the
excess ammonia. Collect the precipitated hydrated
manganese oxide, wash, dry, ignite, and weigh, as
directed on p. 267. Calculate the percentage.

ESTIMATION OF LIME.

Lime may be estimated by Ulk's method (see
pp. 351 to 354) or by the following gravimetric
method :—

Weigh off 1 gramme of the finely - powdered
sample. Dissolve all the soluble constituents in acid.
Oxidise by the action of bromine or ammonium
persulphate. Precipitate the iron, alumina, and
manganese by adding ammonia liquor and boiling.
Collect the residue and precipitate on a filter and
wash with warm water. Remove the beaker con-
taining the solution and set it to boil down.
Place a clean beaker under the funnel and dissolve
the precipitate with acid. Wash all the soluble
constituents into the beaker. Re-precipitate by add-
ing a slight excess of ammonia liquor. Filter and
wash. Add the previous filtrate and washings to the
contents of the beaker. Boil. Add 50 c.c. of hot
ammonium oxalate solution and 20 c.c. of 0·88
specific gravity ammonia liquor. Allow the boiling to
continue for a few minutes. Collect the precipitate
on a filter and treat it as previously directed.

ESTIMATION OF MAGNESIA.

Weigh off 1 gramme of the finely - powdered sample and treat it for the separation of silica, alumina, and manganese, as described for the lime estimation on the previous pages. Add a strong solution of ammonium chloride and precipitate the lime by adding hot ammonium oxalate solution. Collect the residue and precipitate on a filter and wash with warm water. The filtrate and washings will contain all the magnesia except the portion mechanically held among the solids on the filter. This may be recovered by placing a large, clean, conical flask under the filter, dissolving the precipitate, washing the filter, and re-precipitating the iron, alumina, and manganese, again collecting on a filter and washing. Combine the filtrates and washings in the conical flask, heat to about 60° C., add ammonia and ammonium phosphate solution to precipitate the magnesia. The flask should be corked and well shaken for a few minutes to facilitate the formation of a crystalline precipitate, which is collected and dealt with as previously directed.

NOTES ON SAMPLING.

SAMPLING OF IRON ORES.

Sampling an Ironstone Seam.—Where an ironstone seam is of reasonable thickness a complete section should be procured and carefully split into layers. Each layer should be drilled, the drill-hole being of uniform thickness throughout. The drillings should be thoroughly mixed, spread out on a large plate, several portions taken—from each part of the spread sample—and placed on another plate. This selected sample should also be thoroughly mixed and spread, and portions taken from it. A sampling machine may be employed.

The final sample should be well mixed and put into suitable clean, dry bottles, corked, and labelled.

In regular mining practice it is impracticable to get such clean material, but analysis of such a sample will show the best possible result and will form a basis from which to assess the amount of extraneous matter from the pit.

When samples are taken for examination by different analysts, each one takes his own sample from the final lot. Two or more mutual samples are taken, placed in labelled bottles, corked, and sealed with the seal of each. A corresponding label should also be placed *in* each bottle before sealing.

Sampling from Ore Quarries.—Where ore is being taken from mountain sides—as in the north of Spain—it is necessary to take samples from various parts of the working face. The quantity taken from each part should, of course, correspond to the extent of that part. If hard and soft portions have been deposited together, an equivalent quantity of each must, of course, be selected.

The samples taken are broken into smaller pieces and mixed well. They may then be made into a conical heap and the heap quartered. Two or three of the quarters are rejected, the remainder is pounded into still smaller pieces, mixed, and again quartered. These operations may be repeated until a manageable sample is obtained, which is pounded into still smaller pieces and mixed.

Samples are then taken in the usual manner.

When ore exists in well-defined strata, differing considerably in quantity, each layer may be sampled and analysed separately. The thickness of each layer should be measured, and the average composition calculated.

Crushing machines may be used to reduce the size of the larger pieces of the sample.

Large samples of ore may be conveniently pounded on an oblong chilled-iron plate with raised sides and ends. An opening is left in one of the sides or ends by which residues may be swept out. The opening is closed by a metal plate during pounding. Chilled-iron stamps, to which long wood handles can be

affixed, are used for pounding. A bucking arrangement is convenient for pulverising the roughly-pounded sample.

Sampling of Consignment of Ore.—The ore

may be sampled at the ship's side or on arrival at the works. The former place is preferable. According to the capacity of the trucks and the amount of the consignment, samples may be taken from every truck, or, generally, from every second, third, fourth, or fifth truck — with an occasional break in the number. About one-quarter of a lb. per ton of ore may be taken as a sample from a ship's cargo.

On proceeding to sample the ore in one of the trucks a mental estimate should be made of the relative proportion of "fines" and "lumps." Fines should be selected from different parts of the truck and kept on the trowel. Pieces should be broken off several of the lumps, and the broken pieces should be placed on the trowel alongside of the fines and the fairness of the relative proportion judged. If necessary, an adjustment is made by adding to, or taking from one or other lot. Equal quantities should be taken from each truck sampled. Objection may be taken to truck-sampling, as it is possible, especially in consignments sent direct from mines to works in trucks, to "top-dress" the ore in trucks. With ordinary watchfulness, however, this cannot be done while unloading a ship-load of ore.

The samples are placed in small bags or cans and

pounded and quartered as before detailed. Care must be taken to keep the samples in their original moist condition during the time of sampling.

Lots sent by rail from mines are sampled in the works as the ore is laid down. The usual practice, noted above, with regard to selecting relative quantities of fines and lumps must be observed.

American System of Sampling Iron Ores.

In the excellent booklet issued by The United States Steel Corporation for the guidance of their staff full directions are given for sampling. It is directed that samples must be taken uniformly over the surface of the loaded cars by taking a minimum of twelve samples from smaller (25-ton) cars or trucks, or not less than fifteen samples from larger (50-ton) steel cars or trucks. A garden trowel is used for sampling, and, as the trowel and handle are 1 foot long, this makes a handy measure. The samples may be taken in transverse parallel lines or on zig-zag lines, each point of sampling—whether of lumps or of fine—being 1 foot from the next one.

When very lumpy ore is to be sampled a rope net with meshes 18 inches by 18 inches is used. The ropes are knotted where they cross each other. The net is spread over the ore, and if a lump of ore or rock comes directly under a knot a piece about the size of the first joint of the thumb is taken, or an equal amount of fine ore is taken if it occurs under a knot.

Fine ores in a ship's hold are sampled by a sampler armed with a small scoop attached to a long handle taking a spoonful containing a definite amount of ore from each grab as it rises above the deck. In some cases the ore is sampled at regular intervals after the grab has exposed a face.

The directions given in the booklet are very comprehensive and clear.

American practice points to satisfactory sampling of the ore from the capacious ore-carrying ships when about one-half of the cargo has been unloaded. A large sample is then taken.

SAMPLING OF PIG IRON.

Sampling at the Blast Furnace.—If the pig iron is being cast into "pigs" a sample piece may be broken from a pig of the third row from the top, from the middle, and from the third row from the bottom. Or samples may be caught from the runner at regular intervals and cast in smaller moulds made in the pig beds.

If the metal is not cast into pigs, but is used as fluid metal, samples should be caught in a ladle at regular intervals, and cast.

Drillings should be taken from each of these samples, and an equal weight from each should be taken and thoroughly mixed. In some cases of dispute which have come under the notice of the author the differences have mainly arisen through

neglect of this simple precaution. A greater quantity of grey iron had been drilled, because more easily drilled.

Owing to segregation it is difficult to drill a fairly representative sample without much trouble. Drillings taken right through the whole section of the pig —from bottom to top of the thickest part—are said to yield a good average. Where the drillings are all taken from one hole in the face of the fracture, the part selected should be chosen with the view of avoiding the results of segregation, and obtaining a fair average sample.

Sampling of Consignment of Pig Iron delivered in Railway Trucks.—Select two or three pigs from every second, third, fourth, or fifth truck, according to tonnage. Have a piece from each selected pig broken off—some from near an end, some from the centre, and some from intermediate portions. Each should be drilled from the fractured face, drillings being taken from near the top of one, near the bottom of another, near the centre of another, towards one side of another, and so on, the final result showing drill holes from every part of the section. The drillings from each sample should be placed in a separate envelope or small cardboard pill box, and an equal quantity from each should be weighed out and put into the general sample. The general sample should then be thoroughly mixed.

Samples of hard white pig irons must be broken into smaller pieces. These, in turn, are again broken into still smaller pieces, and finally crushed into coarse

powder. For analysis the coarse powder is finely crushed in a hardened steel mortar.

Sampling of Ferro-manganese and Spiegeleisen.—The method given for the sampling of pig iron is also applicable to these products. But as the consignments are of more value and the lots sent in are much smaller, the number of pieces selected from each truck is greater than in the case of pig iron. Pieces should be broken off, and these should fairly represent the proportion of large or small section pigs, runners, &c. The selected pieces should be pounded and thoroughly mixed. A portion should then be withdrawn and further pounded, and from the last the sample for bottling is taken.

Sampling of Iron Castings.—The effects of segregation are well known and fully recognised. Mr. Ridsdale found that "ingot moulds frequently vary from 0·05 per cent. sulphur at the bottom to 0·15 per cent. at the top." This has been recently confirmed by J. Henderson. Drillings taken from near the surface of castings are not trustworthy. Sulphur, due to moulder's blacking, may sometimes be found in abundance near the surface, and it apparently penetrates in diminishing quantity as it advances, as shown by Ainsworth (see the *Iron and Steel Institute Journal*, 1907, I.).

In **steel ingots** there is segregation, and in some large ingots this is considerable. Mr. Talbot has given (*Iron and Steel Institute Journal*, 1905, II.) full details of an enquiry into this important matter.

"Variations of carbon and phosphorus in steel billets" is a subject dealt with by Axel Wahlberg, and detailed in the *Iron and Steel Institute Journal*, 1901, II.

The segregation of sulphur in finished material may be clearly demonstrated by the application of the Baumann auto-sulphur printing method (see p. 389). The other metalloids also in some measure segregate.

All these considerations give point to the observations of Mr. A. Ladd Colby (see the *Iron and Steel Institute Journal*, 1906, III.). "Drilling from a test ingot, cast during pouring, is the only practicable method by which an identified average sample of a heat of steel rolled into rails can be identified. . . . There is an unavoidable variation in the composition of the different rails from each blow, as well as those from each ingot, a difference between the two ends of a rail, and, in point of fact, unavoidable variations even in the different portions of the cross-section. . . . If the average chemical composition of a piece of rail is to be determined, there is only one correct way of obtaining an average sample—namely, to machine-clean dry chips from the entire cross-section of the rail for a uniform depth, weigh the entire sample, dissolve it all in acid, dilute the solution to a known volume, and measure off aliquot portions for the determination of manganese, silicon, and phosphorus; again machine the entire cross-section for a smaller depth, and use all the chips for a gravimetric determination of carbon, preferably by combustion in oxygen; again machine the cross-section, and use all of the sample for the determination of sulphur."

GENERAL NOTES ON LABORATORY OPERATIONS AND APPLIANCES.

Fine-Pounding or Grinding of Samples. — Friable samples are reduced to very fine powder—"impalpable powder"—in an agate mortar with an agate pestle. To facilitate pulverising, the pestle is mounted in a wooden handle with a ferrule, and the mortar is fitted into a recess in a long piece of hard wood. Very small quantities are ground at a time, and they are reduced to the finest state possible by attrition. The finished sample should be absolutely free from gritty particles.

Weighing is conducted on delicate chemical balances. In institutions where balances are used by junior students it is advisable to always test the accuracy of a balance before using.

The amount of sample weighed off for an estimation depends on the percentage of the constituent to be estimated, the process to be followed, the quantity of the finished precipitate, and on other considerations. A sample of steel for the estimation of carbon by colour requires to be weighed off more accurately than a sample of the same steel for the estimation of sulphur. A sample of rich ferro-manganese for the estimation of manganese requires to be weighed off with greater accuracy than a sample of steel for the estimation of phosphorus. To illustrate this point: Consider what would be the result of an erroneous overweighing to the

extent of 0·001 gramme in each of the above instances :—

> 2·001 grammes of steel (containing 0·05 per cent. of phosphorus). Result shown, on the assumption that 2·000 grammes had been weighed out for the estimation, 0·050025 per cent.
>
> 0·501 gramme of ferro-manganese (containing 80 per cent. of manganese). Result shown, on the assumption that 0·500 gramme had been weighed out for the estimation, 80·16 per cent.

In weighing out small quantities of rich substances it is better to finish weighing with the rider than to attempt to weigh an exact quantity. This is specially the case in weighing out copper clippings for standardising, as referred to on p. 176.

Finished precipitates require to be weighed very accurately. In estimating sulphur in steel, for instance, an error of 1 milligramme in the final weighing would cause a serious difference in the percentage returned. Such a wide difference is mentioned here to illustrate : it ought never to occur in practice.

Dissolving.—The weighed sample, in the form of drillings or turnings or in powder of the required fineness, may be dissolved in acid or may require to be fused with a suitable chemical. Iron or steel which cannot be dissolved in strong nitric acid may be dissolved in diluted acid if not too weak.

Sulphuric acid of the usual strength (1·84 specific gravity) is, when diluted, used for dissolving substances which are to be titrated with standard potassium permanganate solution.

Fuming hydrochloric acid—water saturated with gaseous hydrochloric acid—contains 42 per cent. of hydrochloric acid. Its specific gravity is 1·21. As usually sold it is diluted to a specific gravity of 1·16, and it then contains 32·02 per cent. of hydrochloric acid. On prolonged boiling of either of these, acid is driven off till a solution containing 20·2 per cent. of acid is reached. A weaker solution loses water on being boiled. For corresponding notes on nitric acid see p. 409, and on sulphuric acid see p. 416. For dissolving in acids under pressure see p. 253.

Fusing.—The sample is intimately mixed with fusion mixture, potassium bisulphate, sodium per-oxide, or Stead's reagent, and heated in a nickel, platinum, or silver basin or crucible till the contents become fused or liquefied. Heating is effected in a muffle furnace, or over a blowpipe or a Mecker burner. The latter is very convenient. The "melt," as the liquefied mass is called, is allowed to cool and is afterwards dissolved.

Evaporating excess acid, taking down to dryness and baking or roasting, is carried on in basins or beakers over a hot plate.

The hot plate used by the author consists of 4 cast-iron plates, each 50·5 × 22 cm. (about 20 × 8¾ inches), and each having 7 equidistant rows of 35 studs cast on its under side, each stud being 0·5 cm. ($\frac{3}{16}$ inch) deep and 0·5 cm. diameter, and 1·3 cm. apart from each other. A horizontal gas pipe with small burners or jets is laid under each of the plates. The tips of the flames from the

burners envelop the studs, and the plates are heated with a comparatively small consumption of gas. The heat is sufficient to enable the contents of beakers or basins to be evaporated to complete dryness without changing the residues into that condition in which they cannot be dissolved without difficulty. As the plates are 1·3 cm. (about ½ inch) thick they do not warp or buckle.

Beakers or basins containing liquids which are to be evaporated are placed on a directly-heated plate; wash-bottles may be kept warm, or solutions with precipitates may be set to settle, on the adjoining plates without gas-heating. The four plates are set in a frame, and the arrangement, which was first designed for a Staffordshire steel work, was supplied by Messrs. Fletcher, Russell & Co., Warrington, is very useful in a laboratory.

Evaporating to dryness—in order to bring a washed precipitate into condition for weighing—is generally conducted in platinum or porcelain basins on a water bath. The author uses "platinised nickel" basins—basins pressed into shape from compound sheeting composed of two thin platinum sheets hot-rolled with a central sheet of nickel. These were recommended by the late Prof. Dittmar, and are very convenient for rapidly dealing with phospho-molybdate pre-cipitates. The basins are made with ledges for supporting them over suitable-sized openings in the top of the water bath.

Precipitating, Filtering, and Washing.—These are stages in the separating of one constituent from others.

A precipitate is a solid which is almost, but never absolutely, insoluble in the liquid in which it is precipitated. Precipitation should be effected with the view of forming crystals or granules of definite chemical composition capable of being easily separated from the containing liquid when poured on a filter of porous paper and washed. Generally larger crystals or grains are formed in hot liquids than in cold ones. The larger crystals or granules are not so likely to clog the pores of the filter. A more open or porous filter-paper can, therefore, be used, and washing can be done more quickly. On adding cold ammonium oxalate solution to cold calcium chloride solution, an unsatisfactory precipitate (for washing) is formed. If one of the solutions is hot, a better precipitate appears; if both solutions are at the boiling point a still more satisfactory precipitate is obtained. And if, after the addition of the hot precipitant to the hot calcium chloride solution, the liquid containing the precipitate is boiled, a precipitate is found which settles rapidly, and can be quickly washed with satisfactory results.

In some instances, as in the precipitation of magnesium-ammonium-phosphate, the precipitate should be added drop by drop, and each addition should be accompanied by violent agitation. On the other hand, ammonium molybdate solution should be added all at once.

Some precipitates rapidly subside, and filtration is facilitated if the beaker or flask is set aside in a slanting position so as to cause the precipitate to settle at the bottom towards the side from which the liquid will be poured into the filter. A light, flocculent

precipitate, such as the basic hydrate obtained in the course of the gravimetric estimation of manganese, should be filtered off at once, and quickly washed. The gelatinous precipitate of aluminium hydrate should be quickly washed with hot water, and if, through neglect, it happens to become set, further washing is slow and troublesome.

By saturating the filter with hot water immediately before filtering the operation is considerably facilitated.

Washing aims at the removal from the precipitate of the adhering portion of the liquid in which precipitation was effected and of substances dissolved in it. The washing liquid should be of such a nature as not to dissolve more than the unavoidable minimum of the precipitate. A reasonable quantity of the washing liquid should be used, and allowed to drain off before repeating the washing with another like quantity.

The filter should be smaller than the funnel, and the former should not be more than two-thirds full at any time. The washing liquid, ejected from a wash-bottle, should stir up or plough into the precipitate. The filtrate and washings should not be allowed to splash in the collecting beaker.

The filtrate and washings may in some cases be tested (a) to ascertain if sufficient precipitant has been used, and (b) to ascertain if the precipitate has been sufficiently washed. If the filtrate is not required (a) may be ascertained by collecting some of the filtrate in a test-tube and adding a clear solution of some of the substance to be precipitated. Presence of a precipitate in the test-tube is sufficient evidence. To apply test

for (*b*) some of the latter washings may be allowed to drop into a test-tube and a clear solution containing a substance which can cause a precipitate added. Thus, to test if a magnesium-ammonium-phosphate precipitate has been washed enough, a clear acidified solution of silver nitrate is added to some of the last washings collected in a test-tube. If the collected washings contained chlorides a white precipitate of silver chloride will form. Absence of a precipitate is good evidence of thorough washing, but, to be quite safe, it is advisable to wash two or three times more.

When the filtrate is required for further analysis, no portion can be permitted to be withdrawn for testing. But if the power of the measured quantity of precipitating solution is known, and is compared with the weight of the precipitate, a safe inference may be drawn.

When precipitation is properly carried on—with due regard to conditions—filtering and washing may, in most instances, be quickly and efficiently effected in ordinary filters of good filter-paper. Many contrivances are in use for facilitating filtering—such as filter pumps, bell jars and suction pumps, Gooch crucibles (crucibles with bottoms having numerous small perforations) for working with pumps, and asbestos or pulp filters.

Asbestos filters are prepared by igniting fine-fibred asbestos, allowing to cool, placing in a clean mortar along with water, rubbing with a pestle till the fibres are bruised and broken, pouring the pulp produced

into a Gooch crucible, draining till dry (the filter pump being used), and repeating the washing and draining till no more fibres are washed through. For some purposes asbestos washed with acid may be used instead.

Regarding **pulp filters,** the following notes contributed by Ibbotson to "Technics" gives full practical details for preparing and using them as recommended by Horace Jervis (*Chemical News,* 78, p. 257):—

"Ashless filter-paper clippings are torn into small pieces and vigorously shaken in a bottle with considerably more distilled water than they can absorb. In less than five minutes a filtering medium of fine texture is thus obtained. A porcelain filter plate, $\frac{7}{8}$ inch in diameter, and pierced with about twenty holes each nearly $\frac{1}{16}$ inch in diameter, is placed in the throat of a *smooth* funnel of $3\frac{1}{4}$ inches diameter. Closing the stem of the funnel with the thumb of the left hand, water is then poured on in sufficient quantity to fill the stem and cover the plate, care being taken that no air is imprisoned below the latter. Sufficient pulp is then poured on to give a thickness of felting, for ordinary purposes, of no more than a $\frac{1}{4}$ inch; and having adjusted the plate in a horizontal position by means of a glass rod, the thumb is removed and the water allowed to run away, whilst a rotary motion is imparted to the funnel. By means of a spatula or pair of weight pincers, the felting is then pressed slightly and the edge tucked in, so as to prevent a rise of the pulp when liquids are poured on.

"The funnel may then be arranged for suction;

sufficient pressure may easily be induced by the mouth without resorting to the use of a filter pump.

"A precipitate is effectively and rapidly washed by filling up the funnel twice, and after sucking the water from the stem of the funnel, which is full of liquid throughout the filtration, it only remains to transfer the precipitate (which has been rendered sufficiently dry by the suction) to the ignition dish or crucible. This operation does not at first commend itself to the manipulator. By means of a pair of weight-pincers the edge of the pulp is lifted at any point, and the felting folded over about a horizontal diameter, so as to bring the under surface uppermost. This surface is then grasped by the pincers and the whole filter bodily transferred, precipitate side underneath, to the ignition dish, in which a dry piece of ashless paper has been previously placed. The precipitate, which is still moist, does not therefore make actual contact with the platinum. It now only remains to transfer the small amount of precipitate clinging to the sides of the funnel above the region previously occupied by the pulp. The funnel is grasped in the left hand, leaving the thumb free to rotate it by pressure applied at the rim, whilst a small piece of wetted ashless filter-paper is tightly pressed (by means of the thumb only of the right hand) against the side of the funnel. By gradually bringing the paper from throat to rim during the rotation it will be found possible in most cases, after a little practice, to remove every trace of adhering precipitate by means of a small piece of paper.

"The total amount of paper to be burnt off in the

event of its being found necessary to use a second piece for cleaning the funnel is considerably less than the reader might think; and no harm can be done by making absolutely certain of the thorough cleansing of the funnel by the use of still more paper.

"Precipitates of the barium sulphate type are effectually retained by using a thicker layer of pulp, but no advantage over ordinary filter-papers can be claimed for pulp when handling gelatinous precipitates of the zinc sulphide type. .

"**Ignition** may be commenced at once, or at any rate, after rapidly drying at the mouth of the muffle; and when completed, the ignited residue may be entirely brushed from the crucible, of which the weight is therefore not required.

"All precipitates which may be safely ignited in contact with the paper—and their number is considerably greater than a perusal of text-books on quantitative analysis would lead one to suppose—may be treated as described. The extinction of the last spark, which generally takes place in the centre of the mass, is a guarantee of complete and thorough ignition."

Ignition of filter-paper in contact with certain precipitates, such as ammonium-magnesium-phosphate, is at times troublesome unless precautions are taken.

The ignition should be cautiously begun, so as to avoid highly heating the precipitate before the organic part of the filter is burnt away. The precipitate should be white (not grey) before removing the capsule to the hottest part of the muffle, where it should

remain for an hour. Unless this is done, there is danger of the precipitate so clinging to the filter-paper that it becomes difficult to burn off the paper.

When **decomposition** has to be effected—as in the conversion of calcium oxalate into calcium oxide, or the conversion of the hydrated manganese peroxide precipitate to tri-manganic tetroxide—prolonged ignition in a muffle furnace at a high temperature is required. By using a Mecker burner with blast, these changes may be completed in a few minutes. Ignited precipitates must be allowed to cool down in desiccators, otherwise they would absorb moisture from the atmosphere.

Comparing Colour-depths.—In American works the colorimetric estimation of carbon in furnace samples and finished steel is facilitated by various contrivances. The test piece is rolled through a set of small rolls, or is hammered to form a bar about 8 inches × 1 inch × $\frac{1}{2}$ inch, stamped, and allowed to cool on a firebrick slab. It is then placed in a special machine with a horizontal drill. When the skin has been cleared, drillings fall through a funnel into a removable scooped pan which is set on the beam of a delicate balance. The weighing having been quickly completed, and the weighed drillings transferred to a test tube, the measured quantity of nitric acid is dropped in. The test tube is then placed in a bath containing an aqueous solution of calcium chloride, which is kept at its boiling point (110° C.) by high-pressure steam. When the sample is completely dissolved, the test tube is set in a cold-water

vat to cool. The liquid is then transferred to a graduated Eggertz' comparison tube of about 30 c.c. capacity, the upper part of which is bent to an angle of about 115°, and terminates in a small enlargement or funnel. This style of comparison tube facilitates pouring, and the mixing of the contents by shaking.

In comparing depth of colour, the standard Eggertz' tube and the comparison tube are placed in a box or " camera " in a dark room. The camera is blackened within on four sides. Light from an incandescent burner is admitted through a ground-glass plate screened by blue tissue paper. The ground glass disperses the light, and the blue-coloured paper neutralises the yellow rays of light.

For comparing coloured solutions there are several forms of **chromometers.** One of the best known in steel works is that devised by Mr. J. E. Stead for use in estimating carbon in steel, and described by him in the *Iron and Steel Journal,* 1883, vol. i., p. 217. It consists of two parallel measuring tubes of similar diameter, each about 23 cm. (9 inches) long. These are mounted on a suitable frame having graduation marks and carrying a white disc near the bottom and a reflector at the top. A connection can be made between one of the tubes and a wide-neck bottle— generally of about 120 c.c. capacity—for the solution of standard steel. A syringe is also connected (see Fig. 25).

In working with the chromometer a quantity of the solution from the steel to be tested is placed in the left-hand measuring tube. On squeezing the

syringe, the standard solution is forced into the other measuring tube to form a column which will show a corresponding depth of colour. The percentage is then calculated (see p. 10).
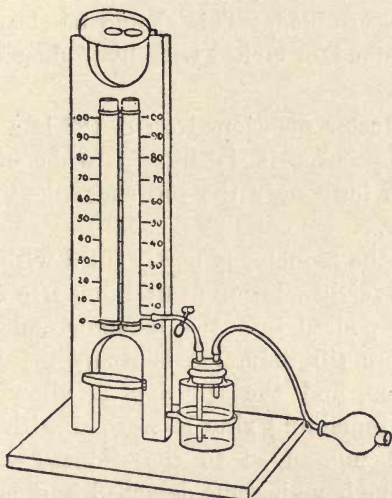
Fig. 25.—Stead's Chromometer.

For volumetric estimations standard solutions and indicators, which readily show a definite " end point," are required. These are fully dealt with in the preceding pages.

For volumetric work, accurately graduated burettes, flasks, &c., may be purchased at very reasonable prices. Pipettes for the estimation of phosphorus in pig iron may be standardised by finding the specific gravity of the solution of pig iron—by means of a 50 c.c. specific gravity bottle—and then finding (by weighing into a

tared beaker) the level in the pipette from which 20·38 c.c. of the solution are delivered. A slip of gummed paper is fastened on the stem, and levels are tentatively marked thereon with pen or pencil. From the result of a few trials the proper level can be easily ascertained. This should be clearly marked with a diamond, or etched with hydrofluoric acid.

The **reductor** mentioned on p. 127 is a glass tube with a stopcock : it is like a wide ungraduated burette. A bulb near the top conveniently increases its capacity.

For use, the reductor is partly filled with pure zinc shot. The ferric solution (containing free acid) to be reduced is poured into the reductor and allowed to remain there till reduction is complete; the tap is then opened, and the solution is allowed to flow out. The remaining zinc is washed with water, the washings being added to the reduced solution. If pieces of zinc have become detached and been carried down with the solution, a little mercuric sulphate (see p. 128) should be added to coat the zinc and prevent further action. Titration may then be proceeded with.

M. R. Baumann's Auto-Sulphur Printing Method.

The piece under investigation must have been filed smooth and polished, and freed from oil and grease.

Mr. Stead * works the method thus :—A piece of smooth - surface bromide paper is soaked in water previously mixed with 3 per cent. of strong sulphuric acid. While still dripping wet the glazed or sensitised side of the paper is placed and evenly pressed upon the polished surface in such a manner as to avoid the imprisonment of any air bubbles. The print is then removed and washed with water to remove sulphuric acid, and, finally, the excess of silver salt is dissolved out with sodium hyposulphite. The print is again washed with water to free from sodium hyposulphite, and it is then ready for mounting. It is only after a little practice that a good, even print can be obtained free from white areas, due to the imprisonment of films of air.

* *Proceedings Staffordshire Iron and Steel Institute,* vol. xxiii., p. 144.

FOR BLAST FURNACE PRACTICE: CALCULA-TION OF YIELD OF ORES, QUANTITIES REQUIRED, &c.

The following factors will be found useful and sufficiently accurate for blast-furnace practice :—

$$°/_\circ \, Fe \times \frac{9}{7} = °/_\circ \, FeO.$$

$$\frac{°/_\circ \, Fe}{0\cdot 7} = °/_\circ \, Fe_2O_3.$$

$$°/_\circ \, FeO \times \frac{7}{9} = °/_\circ \, Fe,$$

$$\text{or} \quad °/_\circ \, FeO \times 0\cdot\dot{7} = °/_\circ \, Fe.$$

$$\frac{°/_\circ \, FeO}{0\cdot 9} = °/_\circ \, Fe_2O_3,$$

$$\text{or} \quad °/_\circ \, FeO \times 1\cdot\dot{1} = °/_\circ \, Fe_2O_3.$$

$$°/_\circ \, Fe_2O_3 \times 0\cdot 7 = °/_\circ \, Fe.$$

$$°/_\circ \, Fe_2O_3 \times 0\cdot 9 = °/_\circ \, FeO.$$

$$°/_\circ \, Si \times 2\cdot 127 = °/_\circ \, SiO_2.$$

$$°/_\circ \, SiO_2 \times 0\cdot 47 = °/_\circ \, Si.$$

$$°/_\circ \, Mn \times 1\cdot 291 = °/_\circ \, MnO.$$

$$°/_\circ \, MnO \times 0\cdot 775 = °/_\circ \, Mn.$$

$$°/_\circ \, P \times 2\cdot 29 = °/_\circ \, P_2O_5.$$

$$°/_\circ \, P_2O_5 \times 0\cdot 437 = °/_\circ \, P.$$

WORKING EXAMPLES.

ABSTRACT OF ANALYSIS OF CLAYBAND IRONSTONE, AND CALCULATION OF ITS COMPOSITION AFTER CALCINATION.

Constituents.	Chemical Formulæ.	I. Composition of the Raw Ironstone.	II. Constituents left after Calculation.	III. Composition of the Calcined Ironstone.
		Per cent.	Units.	Per cent.
Ferrous oxide, . .	FeO	38·50	...	...
Ferric oxide, . .	F_2O_3	2·65	45·43*	63·89‡
Oxide of manganese,	MnO	1·16	1·16†	1·63
Silica, . . .	SiO_2	8·94	8·94	12·57
Alumina, . . .	Al_2O_3	3·56	3·56	5·00
Lime, . . .	CaO	6·15	6·15	8·65
Magnesia, . . .	MgO	3·64	3·64	5·12
Phosphoric acid, .	P_2O_5	2·11	2·11	2·97
Sulphur, . . .	S	0·12	0·12†	0·17
Coaly matter, . .	...	0·43	...	...
Other volatile matter,	...	33·15	...	...
Total, . . .		100·41	71·11	100·00
Iron, . . .		31·80	...	44·72

* When ferrous ores are thoroughly calcined, all the FeO is converted into Fe_2O_3. The percentage of FeO multiplied by 1·1 or divided by 0·9 = percentage of Fe_2O_3.

† MnO, in part at least, is converted into Mn_3O_4. Sulphur would probably partly escape, and partly be converted into SO_3, which would combine with a base or bases present. But the amount of manganous oxide and of sulphur present is not sufficient to seriously affect the calculations.

‡ These and the other figures in column III. are found by dividing the figures in column II. by the sum of that column, and multiplying by 100. Thus, $\frac{45\cdot43}{71\cdot11} \times 100 = 63\cdot89$.

To Find the Percentage of Iron in a Ferric Ore.—
Multiply the percentage of ferric oxide by 0·7.

Example.—An ore contains 73·76 per cent. of ferric oxide.   What percentage of iron does it contain?

   73·76 × 0·7 = 51·63 = percentage of iron.

To Find the Percentage of Iron in a Ferrous Ore.—
Multiply the percentage of ferrous oxide by 0·7̇.

To find the Percentage of Iron in a Cinder containing both Ferrous and Ferric Oxides.—*Find, and sum up, the percentage of iron obtainable from the oxides.*

Example.—A cinder contains 59·67 per cent. of ferrous oxide and 10·59 per cent. of ferric oxide. What percentage of iron does it contain?

$$59\text{·}67 \times \tfrac{7}{9} = 46\text{·}41$$
$$10\text{·}59 \times \tfrac{7}{10} = 7\text{·}41$$

   53·82 = percentage of iron.

To Find the Cost, per Unit of Iron, of Iron in a Material containing a Known Percentage of Iron.—*Divide the number of pence (or cents) per ton by the percentage of iron in the material.*

Example.—An ore containing 53·63 per cent. of iron costs 13s. per ton.   What is the cost per unit?

$$\frac{156}{53\text{·}63} = 2\text{·}91 = \text{pence per unit of iron.}$$

To Find, from the Unit Cost, the Cost of the Ore required per Ton of Pig Iron Produced.—*Multiply the percentage of iron in the pig iron by the price per unit.*

Example.—A pig iron contains 94·5 per cent. of iron and the iron costs 2·91 pence per unit   What is the cost of the iron per ton of the pig iron ?

$$94·5 \times 2·91 = 274·995 = £1\ 2s.\ 11d.$$

To Find, from the Percentage of Ferric Oxide, the Weight of Ore required per Ton of Pig Iron containing a Known Percentage of Iron.—*Divide the percentage of iron in the pig iron by the percentage of ferric oxide in the ore and multiply the product by* 28·586.

To Find, from the Percentage of Ferrous Oxide, the Weight of Ore required per Ton of Pig Iron containing a Known Percentage of Iron.—*Divide the percentage of iron in the pig iron by the percentage of ferrous oxide and multiply the product by* 25·724.

To Find, from the Percentage of Iron, the Weight of Ore required per Ton of Pig Iron containing a Known Percentage of Iron.—*Divide the percentage of iron in the pig iron by the percentage of iron in the ore and multiply the product by* 20.

Example.—An ore contains 52·3 per cent. of iron. How much of it will be required to produce 1 ton containing 94 per cent. of iron?

In this example we have $\dfrac{94 \times 20}{52·3} = \dfrac{1880}{52·3} = 35·946$ cwts. of ore required.

To Find, from the Percentage of Phosphorus and Iron in an Ore, the Percentage of Phosphorus derived from the Ore in the Pig Iron Produced.—*Multiply the percentage of phosphorus in the ore by the percentage of iron in the pig iron and divide the product by the percentage of iron in the ore.*

EXAMPLE.—An ore contains 0·79 per cent. of phosphorus and 36·7 per cent. of iron. What will be the percentage of phosphorus *derived from the ore* in the pig iron (containing 91·5 per cent. of iron) produced ?

$$\frac{0·79 \times 91·5}{36·7} = 1·97 \text{ percentage of phosphorus.}$$

In this and the following examples it is assumed that all the phosphorus will pass into the pig iron.

The percentage of phosphorus derived from the ore may be conveniently calculated from the following :—

$$\frac{\text{Per cent. } P_2O_5 \text{ in the ore} \times 0·56 \times \% \text{ Fe in the pig iron}}{\text{Per cent. FeO in the ore}}.$$

$$\frac{\text{Per cent. } P_2O_5 \text{ in the ore} \times 0·62 \times \% \text{ Fe in the pig iron}}{\text{Per cent. } Fe_2O_3 \text{ in the ore}}.$$

The following examples will serve to show convenient methods for calculating the percentage of phosphorus *due to flux and fuel* in the pig iron.

Phosphorus derived from the Limestone.—10 cwts., containing 0·05 per cent. of phosphoric acid (P_2O_5), were used.

$$\frac{0·05 \times 10}{100} = 0·005 = \text{cwt. of } P_2O_5.$$

0·005 × 0·437 = 0·00218 = cwt. of phosphorus in 10 cwts. of limestone, or 1 ton of pig iron.

Then, if 0·00218 cwt. in 20 cwts. of pig iron, there will be five times that quantity in 100 cwts.

0·00218 × 5 = 0·0109 = percentage of phosphorus in the pig iron, due to the flux.

Phosphorus derived from the Fuel.—22 cwts. of coke, containing 11·34 per cent. of ash, were used. The ash contained 0·041 per cent. of phosphoric acid (P_2O_5).

$$\frac{22 \times 11·34}{100} = 2·495 = \text{cwts. of ash per 20 cwts. of}$$

pig iron.

$$\frac{2·495 \times 0·041}{100} = 0·00102 = \text{cwt. of } P_2O_5 \text{ per}$$

20 cwts. of pig iron.

0·00102 × 0·437 = 0·000445 = cwt. of P per 20 cwts. of pig iron.

0·000445 × 5 = 0·002225 = cwt. of P per 100 cwts. of pig iron.

Collecting all the above into one equation, we have—

$$\frac{22 \times 11·34 \times 0·041 \times 0·437 \times 5}{100 \times 100} = 0·0022.$$

0·0022 = percentage of phosphorus in the pig iron, due to the fuel.

The amount of limestone required for an ore of known composition in order to make a slag containing a given percentage of lime may be calculated as in the following example :—

How much limestone containing 53·2 per cent. of lime and 3·5 per cent. of " refuse " would be required per ton of ore of the undernoted composition to yield a slag containing 52 per cent. of lime ? (The ash of the fuel to be dealt with as a separate calculation.)

	Composition of the Ore. Per cent.	Refuse.
Fe_2O_3,	84·88	...
MnO,	0·25	0·25
SiO_2,	9·00	9·00
Al_2O_3,	0·50	0·50
MgO,	1·00	1·00
CaO,	3·00	...
P_2O_5,	0·03	...
S,	0·04	...
Moisture,	1·30	...
	100·00	10·75

10·75 cwts. of refuse from 5 tons of ore.
3·0 „ lime „ 5 „

As the slag is to contain 52 per cent. of lime, the refuse must be 48 per cent. of the slag.

$$\frac{10·75 \times 52}{48} = \frac{10·75 \times 13}{12} = 11·646.$$

5 tons of ore require 11·646 cwts. of lime.
5 „ contain 3·000 „

Balance, 8·646 „

Lime required for limestone refuse—

$$\frac{3\cdot5 \times 8\cdot646 \times 13}{100 \times 12} = 0\cdot328.$$

$$8\cdot646 \times 0\cdot328 = 8\cdot974.$$

8·974 = cwts. of lime required for 5 tons of the ore.

$$\frac{8\cdot974}{5} = 1\cdot795 = \text{cwts. of lime required per ton of}$$

the ore.

Then, as the limestone contains 53·2 per cent. of lime—

$$\frac{1\cdot795 \times 100}{52\cdot3} = 3\cdot37,$$

each ton of ore will require 3·37 cwts. of the limestone.

PROOF—

Refuse in 5 tons of ore, . . . 10·75
Refuse in the limestone required for
5 tons of ore, ... 0·31

11·06

Lime in limestone, ... 8·974
Lime in ore, ... 3·000

11·974

11·06 × 13 = 143·78, which corresponds $\doteqdot$ to 11·97 × 12 = 143·64.

Calculation of the Weight and Composition of the Slag Produced from a Blast-furnace Charge of Known Composition.

IRONSTONE (68 Cwts. used).

Constituents.	Chemical Formulæ.	Per cent.	Cwts. of Slag-forming Material.*
Ferrous oxide, .	FeO	34·80	...
Silica, . . .	SiO₂	12·50	8·50
Alumina, . .	Al₂O₃	9·50	6·46
Lime, . . .	CaO	5·00	3·40
Magnesia, . .	MgO	3·00	2·04
Manganous oxide, .	MnO	0·50	0·17†
Phosphoric acid, .	P₂O₅	1·25	...
Sulphur, . .	S	0·10	...
Carbon dioxide, .	CO₂	24·35	...
Moisture, . .	H₂O	9·00	...
			0·34 = FeO, &c.
		100·00	20·91

COKE (22 Cwts. used).

Carbon, . . .	C	88·0	...
Ash—Silica, . .	SiO₂	5·0	1·10
Alumina, .	Al₂O₃	3·5	0·77
Lime, . .	CaO	1·0	0·22
Magnesia, .	MgO	0·5	0·11
Sulphur, .	S	1·0	0·22
Moisture, . .	H₂O	1·0	...
		100·0	2·42

* The figures in this column are found by multiplying the cwts. used by the percentage of the constituent, and dividing the product by 100.

† It is assumed that part of the manganous oxide and part of the sulphur goes into the slag.

LIMESTONE (13·5 Cwts. used).

Constituents.	Chemical Formulæ.	Per cent.	Cwts. of Slag-forming Material.*
Lime, ...	CaO	50·40	6·80
Carbon dioxide, . . .	CO_2	39·60	...
Silica, ...	SiO_2	6·00	0·81
Alumina, ...	Al_2O_3	3·00	0·40
Magnesia, ...	MgO	1·00	0·14
		100·00	8·15

Silica in slag-forming materials = 31·26 cwts.
Deduct SiO_2 reduced to Si   = 1·00 ,,

                              30·26 ,,

WEIGHT AND COMPOSITION OF THE SLAG.

Constituents.	Cwts.	Per cent.†
Silica, ...	9·41	30·91
Lime, ...	10·42	34·26
Alumina, ...	7·63	25·07
Magnesia, ...	2·25	7·37
Manganous oxide, ...	0·17	0·56
Iron oxide, sulphur, &c., . .	0·56	1·84
	30·44	100·01

* The figures in this column are found by multiplying the cwts. used by the percentage of the constituent, and dividing the product by 100.

† The figures in this column are found by dividing the percentage by 30·44 and multiplying the product by 100.

NOTES ON PREPARING AND STORING
SOLUTIONS.

Solutions for analytical purposes should be pre-
pared from pure chemicals, and stored in well-stoppered
stock bottles (half-Winchesters suit well for many of
the solutions) in a store-room screened from direct
sunlight and situated in a convenient part of the
laboratory.

The shelves should be arranged at suitable dis-
tances from each other, and the place for each bottle
should be marked by a clearly-printed label carefully
covered with paraffin wax. Each stock bottle should
have a clearly-printed, wax-covered label. The labels
of each row should be arranged on the same level—
those for the top row being placed near the bottom
of the bottles, those for the bottom row near the top,
and those for the intermediate rows placed in inter-
mediate positions, each row differing from the others.
Bottles which are thus symmetrically labelled are
easily kept in their respective places. If, by mistake,
a bottle is placed on a wrong shelf, the error is at once
detected, and its proper place is soon found.

Many of the solutions may be conveniently made
up in stoneware jugs. These are not so tender as
glass ware.

Acetic Acid cooled below 15·5° C. forms large, colourless, transparent crystals. Above that temperature these melt and yield a colourless, pungent liquid known as **glacial acetic acid,** which has a density of 1·063. As usually sold, its specific gravity is 1·045, but the strength of this acid cannot with certainty be ascertained by its density. The weight of dry sodium carbonate required to neutralise a measured quantity is a safer guide.

Arsenious Oxide.—Weigh off 0·66 gramme of pure arsenious oxide (= 0·5 gramme of metallic arsenic) in fine powder, place it in a flask, add 2 grammes of sodium bicarbonate and 100 c.c. of boiling distilled water. Boil the liquid till all the arsenious oxide has dissolved. Allow to cool, add 2 grammes of sodium bicarbonate, and dilute to 1 litre.

Ammonia liquor, or **liquor ammoniæ,** is a solution of gaseous ammonia in water. The higher the percentage of ammonia in solution the lower its specific gravity. As usually sold it has a specific gravity of 0·88 at 15° C. This saturated solution contains 35 per cent.of ammonia.

Ammonium Acetate.—Neutralise 1·045 specific gravity acetic acid exactly with 0·88 specific gravity ammonia liquor, using phenolphthalein or litmus as indicator.

26

Ammonium Chloride.—Dissolve 200 grammes of pure ammonium chloride in hot water, and make up with cold water to 1 litre.

Ammonium Molybdate.—Weigh off 50 grammes of pure ammonium molybdate, stir into 100 c.c. of water, and dissolve in 100 c.c. of 0·88 specific gravity ammonia liquor. Pour the solution into 750 c.c. of *cold* 1·20 specific gravity nitric acid (see p. 410). Stir vigorously, or, by means of a foot-bellows, blow air through the dilute nitric acid while adding the other solution. Allow to settle, and, if necessary, filter through a double close-texture filter into the stock bottle.

J. E. Stead uses (see p. 32) a 10 per cent. solution of ammonium molybdate in water. This is used in conjunction with excess of nitric acid.

Ammonium Nitrate.—Dissolve 2 lbs. of pure ammonium nitrate in warm water, filter the solution if necessary, make up with cold water to 1·5 litres, and mix well.

Two kilogrammes may be similarly treated and made up to 1,650 c.c.

Ammonium Oxalate.—Dissolve 100 grammes of pure ammonium oxalate in 2½ litres of hot water.

Or, dissolve ¼ lb. (113 grammes) in 2¾ litres of hot water. When cool, make up with water to 2,825 c.c. and mix well.

One c.c. of this solution can cause the precipitation of calcium oxalate equal to 0·0177 gramme of lime.

Ammonium Phosphate.—Dissolve 200 grammes of pure ammonium phosphate in 1 litre of warm water. When cool, make up to the 1,000 c.c. mark with cold water and mix well. Or, dissolve ½ lb. (226 grammes) and, when cold, make up with water to 1,130 c.c. and mix well. This solution does not keep well.

One c.c. of this solution can cause the precipitation of ammonium-magnesium-phosphate equal to 0·023 gramme of magnesia.

Ammonium Thiocyanate (Sulphocyanide) for Copper Estimation.—Dissolve 25 grammes of pure ammonium thiocyanate in water, make up to 250 c.c. with water and mix well. This solution does not keep well.

Ammonium Thiocyanate (Sulphocyanide) for Indicator.—Dissolve 2 grammes of the pure salt in 100 c.c. of water. This solution does not keep well.

Aqua Regia.—Mix 3 volumes of 1·16 specific gravity hydrochloric acid with 1 volume of 1·42 specific gravity nitric acid for use when required.

Barium Chloride.—Dissolve 100 grammes of pure barium chloride in about 300 c.c. of warm water. When cool, make up to 1,000 c.c. with cold water and mix well. 10 c.c. of this solution can cause the formation of a precipitate of $BaSO_4$ weighing 0·955 gramme.

Bleaching Powder.—Dissolve, as far as practicable, 35 grammes of bleaching powder in 1,000 c.c. of water. Filter into the stock bottle.

Cadmium Acetate.—Dissolve 25 grammes of pure cadmium acetate in 500 c.c. of water, add 100 c.c. of glacial acetic acid, and make up with water to 1 litre.

Cadmium Chloride.—Dissolve 40 grammes of pure cadmium chloride in 1 litre of water, add 1 litre of 0·88 specific gravity ammonia liquor and mix well.

Caustic Potash.—See Potassium Hydroxide, pp. 411 and 412.

Caustic Soda.—See Sodium Hydroxide, p. 415.

Chromic Acid for Carbon Combustions.—Dissolve 50 c.c. of chromic acid crystals in 90 c.c. of water and add 350 c.c. of 1·51 specific gravity sulphuric acid.

Citric Acid—Concentrated Solution.—Dissolve 250 grammes of chemically pure, non-decomposed, crystallised citric acid in water, add 5 grammes of salicylic acid, and make up with more water to 2½ litres.

Citric Acid—Dilute (2 per cent.) Solution.—Dilute 1 part of the above concentrated solution with 4 parts of water.

Dimethylglyoxime for Nickel Estimation.—Pound some crystals of the salt. Weigh off 2·5 grammes and transfer to a 250 c.c. graduated flask. Add about 220 c.c. of 98 per cent. ethyl alcohol, stopper the flask, and shake it till the salt dissolves. If the alcohol has lost strength there will be much difficulty in dissolving.

On long standing, decomposition may take place.

Ether.—This may be purchased as required. It should be kept in a stoppered bottle with a ground cap.

Ferrous Sulphate—$\frac{N}{10}$ Standard Solution for Volumetric Estimation of Vanadium.—Quickly dissolve 1·39 grammes of pure ferrous sulphate in water, to which about 2 per cent. of pure sulphuric acid has been added. Transfer the solution to a 500 c.c. graduated flask, make up to the mark with water, and mix well. Standardise with standard solution of potassium permanganate.

Ferrous Sulphate—$\frac{N}{20}$ Standard Solution for Volumetric Estimation of Vanadium (p. 223).—Carefully dilute a measured quantity of $\frac{N}{10}$ solution, as above, with an equal quantity of water, and mix well.

Hydrochloric Acid is a colourless gas with a very pungent smell. It is extremely soluble in water. At ordinary temperature and pressure a solution containing 42·9 per cent. of the acid may be obtained. The specific gravity of the saturated solution is 1·212. As usually sold "hydrochloric acid" has a specific gravity of 1·16. When of this density it contains 32·02 per cent. of HCl. Weak aqueous solution of hydrochloric acid loses water when boiled and becomes stronger; a strong solution when boiled loses gas and becomes weaker. In both cases the result is an acid containing 20·24 per cent. of HCl.

Pure hydrochloric acid should be used for analysis.

Hydrochloric Acid of 1·1 Specific Gravity. — To 250 c.c. of 1·16 specific gravity hydrochloric acid add 150 c.c. of water and mix well.

Hydrofluoric Acid.—The aqueous solution of hydrofluoric acid is a corrosive, irritating liquid which readily attacks glass vessels. It is, therefore, kept in gutta-percha bottles, which should be kept carefully closed with gutta-percha stoppers. It is seldom sold in a state of purity, and when a few drops are evaporated in a platinum dish (in a fume cupboard, of course) a solid residue is left. The weight should be ascertained and allowed for as a "blank."

Hydrogen Peroxide.—This may be purchased of the required strength, or may be prepared by triturating barium peroxide with water and adding hydrochloric acid and more water. It may also be prepared by acting on sodium peroxide with nitric acid and water.

Iodine Solution for Arsenic Estimation.—Dissolve 2 grammes of potassium iodide in about 200 c.c. of water. In the iodide solution dissolve 1·7 grammes of re-sublimed iodine. Make up with water to 1 litre and mix well. Keep the solution in a dark place for a few days before standardising.

Iodine solution should be kept from light, as far as practicable, and should be re-standardised twice per week, at least, if in regular use; or immediately before using if three days have elapsed since the previous titration.

For details of standardising, see pp. 193 to 195.

Iodine Solution for Sulphur Estimation.—Weigh off 2 grammes of re-sublimed iodine and dissolve in 50 c.c. of water containing 4 grammes of potassium iodide. When the iodine has dissolved, make up with water to 1 litre and mix well. Standardise, as directed on pp. 48-51, before using. Store the solution in a dark, cool cupboard. If the solution is in regular use, re-standardise every third day. If used occasionally, re-standardise before using.

Iron Solution for "Correction" in Electrolytic Estimation of Nickel.—Dissolve 0·007 gramme of pure iron wire in hydrochloric acid, and make up with water to 1 litre.

Iron Solution for "Correction" in Gravimetric Estimation of Manganese (p. 38).—Dissolve 0·0177 gramme of fine iron wire (pianoforte wire) in hydrochloric acid, and make up with water to 1 litre.

Lead Acetate for Molybdenum Estimation.—Dissolve 10 grammes of pure crystals in about 600 c.c. of water slightly acidulated with acetic acid in a graduated litre flask, make up with water to the mark, and mix well. 20 c.c. of this solution can precipitate 0·05 gramme of molybdenum as lead molybdate.

Magnesia Mixture.—Dissolve 25 grammes of pure magnesium chloride ($MgCl_2,6H_2O$) and 25 grammes of pure ammonium chloride in 400 c.c. of water. Add 200 c.c. of 0·88 specific gravity ammonia liquor and mix well. It is advisable to prepare this solution some time beforehand, and to decant the clear liquid or separate any precipitate which forms by filtration.

One c.c. of this solution may be assumed to be capable of causing the formation of a precipitate of ammonium - magnesium - phosphate containing 0·01 gramme of phosphorus.

Magnesium Citrate.—Place 200 grammes of citric acid, 40 grammes of ammonium chloride, and 200 c.c. of water in a Bohemian flask of 1 litre capacity. Add 500 c.c. of 20 per cent. ammonia liquor. Close the flask with a rubber stopper and allow to remain until the salts have dissolved and the fluid has cooled. Add 55·2 grammes of magnesium chloride, dissolve, and make up with water to 1 litre.

Mercuric Chloride. — Dissolve 25 grammes of mercuric chloride in 500 c.c. of warm water.

Methyl Orange for Indicator.—This solution may conveniently be purchased.

Nitric Acid is a colourless, fuming, corrosive liquid, having a specific gravity of 1·53. As usually sold it is diluted with water till its specific gravity is about 1·42. At 1·42 the solution contains 69·34 per cent. of nitric acid.

When strong nitric acid is boiled it is partially decomposed, nitrogen peroxide and water being formed. When weak nitric acid is boiled, water is driven off. Whatever the strength of the acid, therefore, on being boiled it loses either nitric acid or water until the strength reaches 68 per cent. of NHO_3.

For analytical work pure acid should be used.

Nitric Acid, Dilute, for Carbon Estimation. — Add 200 to 210 c.c. of 1·42 specific gravity nitric acid to 250 c.c. of water and mix well. The specific gravity of the liquid should be about 1·20 when cool. Test with the hydrometer. If required, add either acid or water to correct the density.

Nitric Acid, Dilute, for Volumetric Estimation of Phosphorus.—To 2,500 c.c. of water add 25 c.c. of 1·42 specific gravity nitric acid, and mix thoroughly. The strength of this dilute solution may be ascertained by titrating with standard solution of sodium carbonate. It should also be standardised with the sodium hydroxide solution which is to be used in the phosphorus estimation.

Phenolphthalein for Indicator.—Dissolve 1 gramme of the powder in 300 c.c. of alcohol and add 250 c.c. of water. Add clear, dilute solution of sodium or potassium hydroxide, drop by drop, till the solution becomes pink coloured; then add dilute nitric acid solution till the colour is just discharged. A prepared solution may conveniently be purchased.

Potassium-cupric Chloride.—Weigh off 90 grammes of pure copper-potassium chloride. Place the weighed

portion in a 1,000 c.c. graduated flask along with 50 c.c. of 1·16 specific gravity hydrochloric acid and about 220 c.c. of water. Dissolve the salt, make up to the mark with cold water, and mix well.

Potassium Cyanide—Standard Solution for Nickel Estimation. — This is prepared as directed on pp. 173 to 175.

Potassium Dichromate (Dichrome)—Standard Solution for Volumetric Estimation of Iron.—This is prepared and standardised as directed on pp. 131 to 134.

Potassium Ferricyanide for Indicator. — Dissolve about 0·10 or 0·20 gramme of pure potassium ferricyanide in about 100 c.c. of water. Only freshly-prepared ferricyanide solution should be used.

Potassium Hydrate.—See below.

Potassium Hydroxide (Potassium Hydrate or Caustic Potash) for Combustion.—Dissolve 105 grammes of pure potassium hydroxide in water and make up to 250 c.c. with more water. Keep in a bottle with a tight-fitting cork.

Potassium Hydroxide (Potassium Hydrate or Caustic Potash) for Charging Dufty Tower.— To 200 c.c. of water add 7 sticks (about 80 grammes) of potassium hydroxide. When the solution has cooled transfer it to the Dufty tower.

Potassium Iodide for Nickel Estimation.—Dissolve 20 grammes of pure silver iodide in water, and make up to 1 litre with water.

Potassium Permanganate — Standard Solution for Volumetric Estimation of Iron.—Prepare and standardise as directed on pp. 121 to 125.

Potassium Permanganate for Volumetric Estimation of Phosphorus.—Dissolve 4·264 grammes of potassium permanganate in water, and make up with more water to 1 litre.

Potassium Permanganate for Volumetric Estimation of Vanadium. — Dissolve 6·25 grammes of finely-pounded crystals in water in a beaker and stir well

with a glass rod without a rubber. Cautiously decant into a 250 c.c. graduated flask. If all the crystals have not dissolved add more water. Decant again. Repeat, if necessary. When all the salt has dissolved, make up with water and mix well.

Potassium Permanganate—$\frac{N}{10}$ Standard Solution for Volumetric Estimation of Vanadium. — Place 3·163 grammes of finely-pounded pure crystals in water in a beaker, and stir well with a glass rod without a rubber. Cautiously decant into a 1,000 c.c. graduated flask. If all the crystals have not dissolved, add more water and decant again. Repeat, if necessary. When all the salt has dissolved, make up with water and mix well.

Silver Nitrate for Colorometric Estimation of Manganese in Steel.—Dissolve 1·33 grammes of pure silver nitrate in water, make up to 1,000 c.c. with water, and mix well. Allow to settle, and, if necessary, filter. If, in consequence of the water not being quite pure, there is more than a slight precipitate, more silver nitrate should be added, and the clear solution filtered off. Keep in an amber-coloured bottle or in a dark place.

Silver Nitrate for Colorometric Estimation of Manganese in Pig Iron.—Dissolve 4 grammes of pure silver nitrate in water, make up to 1 litre with water, and mix well. If, on standing, a precipitate settles out, treat as above. Keep in an amber-coloured bottle or in a dark place.

Silver Nitrate for Nickel Estimation.— Dissolve 0·5 gramme of the pure salt in water, make up to 1 litre with water, and mix well. Keep in an amber-coloured bottle or in a dark place.

Silver Nitrate—Standard Solution for Rapid Volumetric Estimation of Nickel.—Dissolve 5·789 grammes of pure silver nitrate in water, make up to 1 litre with water, and mix well. Keep in an amber-coloured bottle or in a dark place.

Silver Nitrate for Testing Washings.— Dissolve 2 grammes of silver nitrate in 500 c.c. of water, add 500 c.c. of 1·42 specific gravity nitric acid. Allow to stand for a little, and, if necessary, filter. Keep in an amber-coloured bottle or in a dark place.

Sodium Hydrate.—See Sodium Hydroxide on next page.

Sodium Hydroxide (Sodium Hydrate or Caustic Soda) for Sulphur Estimation.—Dissolve 56 grammes (or 2 ozs.) of pure sodium hydrate in 1 litre of water Allow to stand for some hours, and, if any sediment has formed, separate the clear portion of the solution by decantation.

Sodium Hydroxide (Sodium Hydrate or Caustic Soda) for Volumetric Estimation of Phosphorus.—(*a*) Stock solution. Dissolve 68 grammes in water, and, when cold, make up with water to 1,000 c.c. (*b*) Working solution. Draw off 250 c.c. of the stock solution, make up with water to 2½ litres, and mix thoroughly.

Sodium Thiosulphate (Sulphocyanide) for Aluminium Estimation.—Dissolve 90 grammes of pure thiosulphate in 50 c.c. of hot water. Filter if necessary. This solution does not keep well.

Stannous Chloride (Strong).—To 15 c.c. of water add 30 grammes of pure stannous chloride and stir for a few minutes. Add 450 c.c. of 1·16 specific gravity hydrochloric acid. Continue the stirring to dissolve as much as possible of the salt. If an insoluble residue remains, allow it to settle. Pour off the clear liquid into a suitable bottle. Store in a cool, dark cupboard. On long standing a precipitate of stannic chloride sometimes forms.

Stannous Chloride (Dilute).—Measure off 10 c.c. of the strong stannous chloride solution, make up to 100 c.c. with water, and charge into the dropper for finishing reduction of ferric solutions.

Starch Solution.—Make 1 gramme of potato starch into a thick cream with a little cold water by stirring in an 18 cm. (about 7 inches) diameter porcelain basin. Quickly pour into the cream 500 c.c. of boiling water while stirring vigorously. Boil the solution for two or three minutes, and allow it to cool before using. A starch solution prepared in this manner may remain in good condition for a few days.

Sulphuric Acid is a heavy, oily, colourless liquid, which when strong and pure has a specific gravity of 1·854. When boiled it is decomposed, and gives off sulphur trioxide, as indicated by the equation, $H_2SO_4 = SO_3 + H_2O$, until 1·5 per cent. of water is present, after which it distils unchanged.

As usually sold, its specific gravity is 1·84. This strong acid should be cautiously diluted by pouring into water.

Sulphuric acid sold as "pure" sometimes contains lead in solution, which separates on dilution.

Sulphuric Acid, Dilute No. 1 (sp. gr. 1·51), for the Estimation of Vanadium.—Cautiously pour 500 c.c. of 1·84 specific gravity sulphuric acid into a Bohemian flask containing 500 c.c. of water. Allow to slowly mix and cool. If a precipitate has settled out decant the clear portion of the solution into the stock bottle. Keep in a well-stoppered bottle.

Sulphuric Acid, Dilute No. 2 (sp. gr. 1·26), for Dissolving Steel.—Cautiously pour 250 c.c. of 1·84 specific gravity sulphuric acid into 750 c.c. of water. Allow to settle for some days. Pour off from any settled precipitate into a bottle with a well-ground glass stopper.

Sulphuric Acid, Dilute No. 3, for use in Rapid Estimation of Lime (p. 353).—Cautiously pour 250 c.c. of 1·84 specific gravity sulphuric acid into 1 litre of water. Allow to settle for some days. Pour off from any settled precipitate into a bottle with a well-ground stopper.

Sulphuric Acid, Dilute No. 4, for Use in Sulphur Estimations. — Cautiously pour 100 c.c. of 1·84 specific gravity sulphuric acid to 1 litre of water. Allow to settle for some days. Pour off from any settled precipitate into a bottle with a well-ground glass stopper.

Sulphuric Acid, Dilute No. 5, for Dissolving Iron Ores. — Cautiously pour 60 c.c. of 1·84 specific gravity sulphuric acid to 950 c.c. of water. Allow to settle for some days. Pour off from any settled precipitate into a bottle with a well-ground glass stopper.

Sulphurous Anhydride or Sulphurous Acid.—Syphons containing water highly charged with this gas may be purchased. When the charged syphon is in an upright position, gaseous anhydride will be delivered on opening the tap. But when the charged syphon is laid horizontally, the anhydride in aqueous solution will be delivered on opening the tap. 5 or 10 per cent. aqueous solutions may also be purchased.

Zinc Chloride.—Dissolve 100 grammes of pure zinc chloride in 1 litre of water.

NOTES ON SOME SOLID REAGENTS.

Ammonium Persulphate.—In order to get a sharp reaction on the addition of this reagent, it is necessary that it should be slightly moistened a few hours before being used. If moistened a day or two beforehand, a sharp reaction may be had.

Fusion Mixture.—This is composed of about 6 parts of dry pure potassium carbonate with 5 parts of dry pure sodium carbonate. The mixture may be purchased.

Sodium Peroxide.—This very active reagent, which readily absorbs moisture, is sold in sealed boxes. If transferred to a glass-stoppered bottle the inside of the neck should be carefully wiped with a piece of filter paper before closing with the stopper.

Stead's Tribasic Reagent consists of 20 parts of pure lime or magnesia, 5 parts of potassium carbonate, and 5 parts of sodium carbonate. This is a useful fusion mixture. The two carbonates, soda and potash, when mixed, melt at a lower temperature than when separate, and the magnesia, being infusible, keeps the mass porous and open to oxidation.

SUPPLEMENT.

The following methods from the booklet on the Commercial Analysis of Iron Ores of the United States Steel Corporation are included here by kind permission of the Corporation, per J. M. Camp, Chairman of the Chemists' Committee:—

IRON.

By the Bichromate or Permanganate Methods.

One or more portions of one-half to one gram of the ore are placed in a beaker, and 5 to 10 c.c. of the solution of stannous chloride and 5 to 25 c.c. of strong hydrochloric acid are added. This variation in the amount of acid is due, aside from the variations in the weight of sample and the varying solubilities of the ores, to the fact that while in the permanganate method the minimum amount of free acid should be present, with the bichromate method an excess of acid is essential. The beaker is covered with a watch-glass and heated gently on the steam bath, or hot plate, until all iron is dissolved, and if the permanganate method is to be used, the volume of the solution is reduced by evaporation so as not to exceed 10 c.c. While still hot the stannous chloride solution is added from a burette, drop by drop, until the color due to the ferric chloride just disappears, and then one drop

in excess. The solution is diluted to about 350 c.c. with cold water, 5 c.c. of mercuric chloride solution are added and the solution is thoroughly stirred. From this point the bichromate or permanganate titrations are optional. In the former case, the potassium bichromate solution is added from a burette until a drop of the solution being titrated, added to a drop of the potassium ferricyanide solution on a paraffined plate shows no ferrous iron. In the latter case, 10 c.c. of the titrating solution are added for a one-half gram sample, and 20 c.c. for one gram. The solution is stirred and titrated with the potassium permanganate. In either case, the number of c.c. used multiplied by the respective factor gives the percentage of iron.

If the residue is suspected of containing iron it is filtered off, ignited and fused; the fusion is dissolved in water, acidified with hydrochloric acid, and the solution reduced and titrated as above ; or the solution before being acidified is filtered, the ferric oxide on the filter is dissolved in hydrochloric acid and added to the main solution or titrated separately.

SOLUTIONS FOR IRON TITRATIONS.

The stannous chloride solution is made by dissolving 250 grams of the salt in 500 c.c. of strong hydrochloric acid, and diluting to 1,000 c.c.

The mercuric chloride solution is saturated in the cold.

The potassium ferricyanide solution is made fresh each day by dissolving in the proportion of 0·100 gram of the salt in 100 c.c. of water.

The potassium bichromate solution is made by dissolving the salt in the proportion of about 8·9 grams to one liter of water, and standardising with an iron ore, iron wire or steel, of known iron content. One c.c. equals approximately 1 per cent. iron with a one gram sample taken for analysis.

The titrating solution is made up in the following proportion to the liter : 90 grams of manganous sulphate are dissolved in 650 c.c. of water, 175 c.c. of strong sulphuric acid are added, then 175 c.c. of phosphoric acid of 1·75 sp. gr., and the solution is filtered if necessary.

The permanganate solution is made by dissolving the salt in the proportion of about 5·7 grams to one liter of water and standardising in the same manner as the bichromate solution. One c.c. equals approximately 1 per cent. iron with a one gram sample taken for analysis.

SILICA.

Using one gram with Hydrofluoric Evaporation.

One gram of the sample is transferred to a porcelain dish, or a beaker, with watch-glass cover, and 20 c.c. of strong hydrochloric acid are added. A gentle heat is applied until the ore is dissolved and the solution is then evaporated to dryness, unless it has been conclusively shown to be unnecessary.* To the residue, which should not be heated above

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* This clause is introduced on the insistence of the mine chemists that with certain ores evaporation to dryness is not necessary to obtain all the silica.

120° C., 15 c.c. of dilute hydrochloric acid (1 part acid to 1 part water) are added, heat is applied until the salts are dissolved and the solution is diluted with hot water. The precipitate is filtered off, washed, ignited at the highest temperature of the blast lamp or muffle furnace for at least five minutes, cooled and weighed. To the residue in the crucible one or two drops of strong sulphuric and 5 c.c. of hydrofluoric acids are added, and the solution is evaporated to the expulsion of sulphuric acid. The residue is ignited as before and again weighed ; the difference between the two weights is silica.

SILICA.

Using one to five grams when all or part of the Filtrate is used for the Phosphorus or other Determinations.

One to five grams of the sample are transferred to a dish (beaker optional) with a watch-glass cover, 20 to 50 c.c. of strong hydrochloric acid are added, and a gentle heat is applied, without boiling, for about one-half hour. The solution is diluted with an equal volume of water, filtered into another dish of the same size, and the visible iron stain is washed out of the filter paper. This solution containing the bulk of the iron is allowed to go to dryness on the steam bath. The residue is ignited in a platinum crucible, and then fused with about six times its weight of sodium carbonate. The fusion may be leached out of the crucible, but it is found more expeditious to let it cool around the end of a platinum rod, and on again heating the crucible the entire mass adhering to the

rod is removed. It is then dissolved in the original filtrate, or placed while still hot in the covered dish, in which the original solution was made and to which about 25 c.c. of hot water have previously been added. The small amount remaining in the crucible is dissolved in hot water, and finally in hot dilute hydrochloric acid (1 part acid to 1 part water), and added to the dish containing the fusion, which by this time has been disintegrated by the hot water and acidified with hydrochloric acid; this dish is then placed with the other on the steam bath. When the contents of both dishes are dry, 10 to 15 c.c. of strong hydrochloric acid are added to the dish containing the residue of the original filtrate. After heating until the ferric salt is dissolved, the solution is evaporated until the excess of hydrochloric acid is expelled, as is indicated by the first appearance of insoluble ferric chloride on the bottom or sides of the dish. Seven c.c. of strong nitric acid are added and heat is applied for about one minute, or until the violent reaction is over. The solution is diluted with cold water and filtered into a suitable flask. This is the procedure if all the filtrate is to be used for the phosphorus determination; but the evaporation of the excess hydrochloric acid and the addition of the nitric acid are dispensed with, if the united filtrates are to be received in a volumetric flask and aliquot portions taken for the other determinations.

To the dish containing the fusion, and which should not be heated above 120° C., just enough dilute hydrochloric acid is added to moisten the residue. Hot water is then added and heat applied until all the

salts are dissolved, when the solution is filtered into the same flask with the last filtrate; the combined filtrates should not exceed 150 c.c. if the solution is to be used for the phosphorus determination. In this case, the complete washing of the silica is continued in another flask until free from chlorides, and these washings are discarded. The filter and its contents are then ignited and weighed as silica. The filtrate in the flask is reserved for the phosphorus determination, or if in a volumetric flask, for the determinations which follow.

PHOSPHORUS.

By the Fusion Method.

For this determination five grams of the sample are taken for all ores when the phosphorus contents are under 0·100 per cent., two and one-half grams when the phosphorus contents are between 0·100 and 0·200 per cent., and one gram when the phosphorus exceeds 0·200 per cent.

An aliquot part of the filtrate, the volume of which should not exceed 150 c.c., representing one gram, or two and one-half grams of the sample, from the five gram portion for silica in the volumetric flask, is boiled in a suitable flask for a few minutes with the addition of 10 c.c. of strong nitric acid. To this solution, or to the entire filtrate in the flask from the five gram portion, a slight excess of strong ammonia is added over the amount necessary to precipitate the iron and alumina, and after mixing enough

strong nitric acid to dissolve the precipitate with from 5 to 10 c.c. in excess.

The solution is heated to a temperature of 80° C., 50 c.c. of the solution of ammonia molybdate are added, and the flask is shaken continuously for five minutes. The solution is allowed to stand until the precipitate has subsided. If the yellow precipitate is to be weighed, it is caught on a 9 cm. filter-paper that has been dried for at least half an hour at 110° to 120° C. and weighed between watch-glasses, washed thoroughly with a 2 per cent. solution of nitric acid, dried for one hour at the above temperature and weighed between glasses ; 1·63 per cent. of its weight is phosphorus.

If the yellow precipitate is to be titrated by the acid alkali method, the weighing of the filter is dispensed with, the washing with the 2 per cent. nitric acid is continued as before to the complete removal of the iron and molybdenum salts, and then with a 1 per cent. solution of potassium nitrate until free from acid. The filter and its contents are then transferred to a small flask or beaker and an excess of the standard alkali added. When the precipitate is all dissolved by shaking or stirring, about 150 c.c. of water and a couple of drops of a saturated solution of phenolphthalein in alcohol are added, and the solution is back titrated with the standard nitric acid to the disappearance of the color. It is optional to again add the standard alkali, the end point being a faint, permanent pink color.

The yellow precipitate may also be dissolved in

dilute ammonia, and the phosphorus determined by the permanganate titration method as subsequently described. Or it may be dissolved in a hot ammoniacal citrate solution and the phosphorus precipitated as ammonium - magnesium - phosphate, as hereafter described.

Ammonium Molybdate Solution.—This solution is made in the following proportions :—To 225 grams of pure molybdic acid in a suitable flask there is added 500 c.c. of water, and then 500 c.c. of strong ammonia. When in solution, this is poured into a flask containing 2,500 c.c. of nitric acid of $1 \cdot 20$ sp. gr., the solution being kept agitated, and three or four drops of ammonium or sodium phosphate solution are added to coagulate the suspended impurities. The solution is kept in a warm place over night or until the supernatant liquid is clear, when it is filtered into a bottle for use.

Stock Solution of Caustic Soda.—145 grams are dissolved in water and the solution is diluted to 2,200 c.c.; 200 c.c. of this solution diluted to 2,000 c.c. will be of approximate strength.

Nitric Acid.—Twenty c.c. of strong nitric acid are diluted to 2,000 c.c. These solutions are made exactly agreeing, and standardised on steels or ores of known phosphorus contents, so that each c.c. used corresponds to $0 \cdot 01$ per cent. phosphorus, when two grams of the sample are used. This weight has been found the most convenient for steel analysis, and a simple calculation enables it to be used for varying weights of either steel or ore.

PHOSPHORUS.

Direct Determination of the Soluble Phosphorus using the Permanganate or the Acid Alkali Titration.

This method is particularly applicable to ores wherein all or a fairly constant proportion of the phosphorus is soluble in strong acid. The insoluble phosphorus is determined at less frequent intervals, and the amount so obtained added to the soluble gives the total phosphorus.

From one to five grams of the sample, according to the phosphorus content, are placed in a beaker with a watch-glass cover, 20 to 50 c.c. of strong hydrochloric acid are added, and a gentle heat is applied until the ore is dissolved. Two or three drops of nitric acid are added, and the solution is boiled a minute or two, and then the excess acid evaporated. The solution is diluted and filtered, the filtrate being received in an 8 to 16 ounce Erlenmeyer flask; the filter and residue are washed with dilute hydrochloric acid (1 part acid to 4 parts water) and water until free from iron discoloration.

Strong ammonia is now added until a slight precipitate persists, or until the iron is completely precipitated, and in either case this is dissolved with strong nitric acid, too great an excess being avoided. The solution is heated to 80° C., 30 to 50 c.c. of ammonium molybdate solution are added, the flask is shaken and placed in a warm place to allow the precipitate to subside. The greater part of the supernatant liquid is siphoned off, the remainder being filtered, or the entire solution is filtered. The pre-

cipitate is washed with ammonium sulphate solution or a 2 per cent. sulphuric acid solution, until free from iron and molybdenum salts.

The funnel containing the precipitate is transferred to the flask in which the precipitation was made, and the precipitate dissolved in dilute ammonia (1 part ammonia to 3 parts water); the resulting solution should not exceed 25 c.c. Eight grams of granulated zinc (20 mesh) are added; then 75 c.c. of sulphuric acid (1 part acid to 4 parts water), and the solution is boiled gently until reduction is complete. It is then filtered through glass wool or cotton, the filtrate being received in a beaker, and the flask and filter are washed thoroughly with cold water. The solution is titrated with potassium permanganate until a slight, permanent, pink tint is obtained. From the number of c.c. used, the percentage of phosphorus is calculated.

If the acid alkali titration is to be used, the yellow precipitate is washed as before with a 2 per cent. nitric acid solution until free from iron and molybdenum salts, then with a 1 per cent. solution of potassium nitrate until free from acid, and the determination is completed in the regular manner.

Solutions.

Standard Permanganate—

204·5 grams potassium permanganate,
1   carboy (48 liters) distilled water.

Ammonium Sulphate—

40,000 c.c. distilled water,
1,100 c.c. ammonium hydrate, sp. gr. 0· 96.
960 c.c. sulphuric acid, sp. gr. 1·84.

Ammonium Molybdate—

    300 grams molybdic acid dissolved in

    1,200 c.c. ammonium hydrate, sp. gr. 0·96.   This
        to be added slowly to

    4,500 c.c. nitric acid, sp. gr. 1·20, keeping the
        solution agitated.

Phenolphthalein—

    Saturated solution in alcohol.

PHOSPHORUS.

By Ignition of the Insoluble Residue.

One to five grams of the sample in a porcelain dish, with watch-glass cover, are digested in 20 to 50 c.c. of strong hydrochloric acid with the aid of a gentle heat.   After diluting slightly with cold water, the solution is filtered into another dish of the same size and the precipitate washed free of the visible iron discoloration.   The filtrate is rapidly evaporated and while this is in progress, the residue is transferred to a platinum crucible and ignited in a muffle furnace or over a blast lamp.   The residue is broken up, re-ignited for a few minutes, then transferred into the original filtrate, and the solution is evaporated to dryness.

Fifteen c.c. of strong hydrochloric acid are now added, and the solution is evaporated until ferric chloride begins to separate in the solid state.   To the covered dish 7 c.c of strong nitric acid are added and heating is continued for about one minute.   The solution is diluted with cold water and filtered into a suitable flask.   The filter and precipitate are washed

with a 2 per cent. nitric acid solution until the iron discoloration is removed.

With unknown ores, and at regular intervals with all ores, as a check, the insoluble residue is fused with sodium carbonate. The fusion is dissolved in dilute hydrochloric acid (1 part acid to 1 part water), and the solution is evaporated to dryness. The residue is redissolved in dilute hydrochloric acid and the solution is filtered into the main filtrate, which has also been evaporated to dryness, and the residue treated as described in the previous paragraph after the evaporation to dryness. The filtrate or the combined filtrates in the flask are made ammoniacal, and the precipitate is dissolved in strong nitric acid with 5 to 10 c.c. in excess. The solution is brought to a temperature of 80° C., 50 c.c. of ammonium molybdate solution are added and the flask is shaken for five minutes.

When the precipitate has subsided, it is filtered off and washed with a 2 per cent. solution of nitric acid. From this point the yellow precipitate may be weighed, or titrated by the acid alkali or permanganate methods as previously described, or dissolved, reprecipitated, and weighed as magnesium pyrophosphate in the following manner.

The yellow precipitate is dissolved on the filter with hot ammonium citrate solution (175 c.c. strong ammonia to 325 c.c. water containing 25 grams citric acid), the filtrate being received in a No. 0 beaker. The filter is washed several times with hot water, then 5 to 10 c.c. of magnesia mixture (100 grams magnesium sulphate plus 300 grams ammonium

chloride in 800 c.c. hot water plus 400 c.c. strong
ammonia) are poured through the filter. The filtrate
in the small beaker is thoroughly mixed and allowed
to stand for at least three hours, and if possible over
night. The precipitate is filtered off, washed with
dilute ammonia (1 part ammonia to 4 parts of water),
ignited at a low temperature until the carbon of the
filter is destroyed, then at the highest temperature
of the muffle furnace or burner, cooled and weighed
as magnesium pyrophosphate containing 27·84 per
cent. phosphorus.

PHOSPHORUS.

When Titanium is Present.

Two grams of the sample are intimately mixed
with eight to ten times its weight of sodium carbonate
in a large platinum crucible and fused over a blast
lamp, the fusion being maintained at the highest
temperature for fifteen to twenty minutes. The
fusion is then transferred to a beaker containing hot
water and thoroughly disintegrated ; the solution is
then filtered and the residue washed with hot
water, or preferably with a 1 per cent. solution of
sodium carbonate. As an extra precaution not deemed
necessary in everyday work, the residue may be
ignited until the filter is destroyed, crushed in the
crucible, fused, disintegrated and filtered off as before,
the filtrates being combined. The filtrate or the com-
bined filtrates are acidified with hydrochloric acid and
evaporated to dryness. The residue is moistened with
dilute hydrochloric acid, dissolved in hot water and
the solution filtered into a suitable flask.

28

The filtrate is made ammoniacal, then strong nitric acid is added with from 5 to 10 c.c. in excess. The solution is brought to a temperature of 80° C., 50 c.c. of ammonium molybdate solution are added, the flask is shaken for five minutes, and the phosphorus determined by any of the methods previously described.

When it is desired to separate the phosphorus from the large amount of sodium salts in the filtrate after the evaporation to dryness, a weighed amount of iron, about 0·05 gram, of known phosphorus content, and in the ferric condition, is added and precipitated in the hot solution with ammonia. The precipitate is filtered off, dissolved in warm, dilute nitric acid, and if the resulting filtrate is somewhat cloudy from particles of filter paper in suspension, and it is desired to remove them, it is refiltered after the addition of a little paper pulp. This filtrate is now made ammoniacal, 5 to 10 c.c. excess nitric acid are added, and the determination is completed as above described.

ALUMINA.

Phosphate Method.

For this determination the hydrochloric acid filtrate from the silica of one gram of the sample, or the hydrochloric acid solution of the precipitated iron and alumina from the gravimetric determination of manganese is used. To the cool solution diluted to about 400 c.c. in a No. 5 beaker, 30 c.c. of a 10 per cent. solution of ammonium phosphate are added, and then ammonia until a faint permanent precipitate is

formed. One and one-half c.c. of strong hydrochloric acid are now added, the solution is stirred until the precipitate is dissolved, and 50 c.c. of a 20 per cent. solution of sodium hyposulphite are added. The solution is heated just to the boiling point, at which 8 c.c. of strong acetic acid and 15 c.c. of a 20 per cent. solution of ammonium acetate in the same measure are added, and the boiling is continued ten minutes. The precipitate is allowed a few minutes to subside, is filtered off as quickly as possible and washed ten times with hot water. The filter and its contents are ignited at a low temperature until the carbon is destroyed, then at the highest temperature of the muffle furnace, cooled and weighed as aluminium phosphate, 41·85 per cent. of which is alumina.

ALUMINA.

Ether Method.

One to five grams of sample are placed in an 8-ounce beaker and dissolved 20 to 50 c.c. of strong hydrochloric acid with the aid of a gentle heat. The solution is diluted and filtered, the residue washed, and the filtrate evaporated to dryness. The residue on the filter is ignited in a platinum crucible, 2 to 6 drops of sulphuric (1 part acid to 1 part water) and 5 to 10 c.c. of hydrofluoric acids are added and the solution is evaporated to dryness. The residue in the crucible is fused with one-half to two and one-half grams of potassium or sodium bisulphate and dissolved in 10 c.c. of dilute hydrochloric acid (1 part acid to 1 part water). The residue from the original filtrate,

after its evaporation to dryness, is dissolved in 20 to 30 c.c. of hydrochloric acid, 1·13 sp. gr., cooled and transferred to a separatory funnel, 40 to 100 c.c. of ether are added and the funnel is shaken for one minute, the solution being kept cool. The acid layer is drawn off into an 8 ounce beaker, and to this is added the solution obtained from the treatment of the insoluble residue. The combined solutions are heated until the ether is driven off, a few crystals of sodium or potassium chlorate are added, and the heating is continued until free chlorine is expelled. The solution is diluted to about 75 c.c., ammonia is added until a slight precipitate persists, then 10 c.c. of a 20 per cent. solution of ammonium acetate. The solution is boiled about one minute and filtered ; the precipitate is washed with hot water, then dissolved in warm dilute hydrochloric acid. After being diluted to about 75 c.c. and a slight excess of ammonia added, the solution is boiled, filtered, and the precipitate washed as before. The combined filtrates are reserved for the determination of manganese, lime, and magnesia. From this point the alumina may be determined by either of the following methods : —

The precipitate is ignited, and weighed as oxides of iron, alumina, and phosphorus. The ignited oxides are dissolved in 3 c.c. of stannous chloride and 10 c.c. of strong hydrochloric acid, and the iron is titrated with a weak bichromate solution, 1 c.c. of which is equal to 0·2 per cent. iron. Or the precipitate is fused with sodium carbonate, the fusion is dissolved in hydrochloric acid, and the iron titrated as above. The

iron calculated as the sesquioxide, plus the phosphorus as pentoxide, is deducted from the total weight of the precipitate leaving the alumina.

Or the filter and precipitate are ignited at a low temperature until the carbon is destroyed. The precipitate is crushed in the crucible and thoroughly fused with about 5 grammes of sodium carbonate. The fusion is dissolved in hot water, a little paper pulp is added to reduce any manganese that may be present, the residue is filtered off and washed. The filtrate received in a small beaker is acidified with hydrochloric acid, heated to boiling, and ammonia is added in slight excess. After boiling for a minute or two, the precipitate is filtered off, washed with hot water, ignited and weighed. This weight minus the weight of the phosphorus as pentoxide is alumina.

MANGANESE.

Gravimetric Method.

The filtrate from the one gram portion for silica, or an aliquot part of the filtrate, equal to one gram of the ore, from the five gram portion for silica in the volumetric flask, is boiled for a few minutes in a No. 5 beaker with the addition of 10 c.c. of strong nitric acid. A basic acetate separation is then made as follows :—The solution is diluted with cold water to about 150 c.c., and the greater part of the free acid is neutralised with strong ammonia, then cautiously with dilute ammonia (1 part ammonia to 4 parts water) with vigorous stirring until a faint precipitate

persists. The solution is then diluted with hot water to about 400 c.c., 25 c.c. of a 20 per cent. solution of ammonium acetate are added, the solution is heated to boiling and boiled about one minute. After the precipitate has subsided, the solution is filtered through a 185 mm. filter on a 4-inch ribbed funnel into a No. 6 beaker.

When the manganese is under 1 per cent. only one basic acetate separation is made and the precipitate is washed several times with hot water. If over one per cent. the precipitate is washed but once, then dissolved on the filter in hot, dilute hydrochloric acid, and the basic acetate separation made as before, except that the dilution before precipitating need not be so great. The filtrate and washings, or the combined filtrates in this determination, or from the iron and alumina in the ether alumina method are heated to boiling and 25 c.c. of strong ammonia added, and then cautiously about one gram of ammonium persulphate. One gram is sufficient to precipitate the manganese in any iron ore. The solution is boiled about ten minutes and the precipitate filtered off, washed with hot water, ignited at a gentle heat and then at the highest temperature of the muffle furnace or blast lamp, and weighed as mangano-manganic oxide, containing 72·05 per cent. manganese. This precipitate may be dissolved before or after ignition, reprecipitated, and weighed as manganese pyrophosphate.

The ignited precipitate of mangano-manganic oxide is usually contaminated with a small amount of silica sufficient to cause an appreciable error in a small percentage of manganese. In this case it is dis-

solved in the crucible in warm, dilute hydrochloric acid ; the residue, if any, is filtered off, washed, burned and the weight obtained is deducted from the previous weight.

The precipitate of iron and alumina on the filter obtained in this determination is to be retained for the determination of alumina by the phosphate method.

MANGANESE.

Volhard's Method.

One to two grams of the sample are placed in a No. 2 beaker with cover, 15 to 25 c.c. of strong hydrochloric acid are added, and heat is applied until the ore is dissolved. Five c.c. of nitric acid or a few crystals of potassium chlorate are now added, and the solution is boiled until nitrous fumes or free chlorine are expelled. Evaporation is continued to the expulsion of free acid, the solution is diluted to about 100 c.c. and washed into a volumetric flask. Zinc oxide emulsion is added in excess, the solution is diluted to the mark and mixed thoroughly ; the precipitate is allowed to subside and an aliquot portion is decanted off, equal to one-half or one gramme of the ore. For ores low in manganese the solution is made slightly turbid with zinc oxide emulsion to coagulate the manganese dioxide set free in the titration. The solution is heated to boiling and titrated with permanganate until a faint, pink color persists. Or, after the dilution to about 100 c.c., the solution is washed into a half liter flask, an excess of zinc oxide emulsion is added as before, the solution is heated to boiling

and titrated directly in the presence of the iron precipitate.

Strength of Permanganate Solution for Iron Ores. —One c.c. equals 0·1 per cent. manganese, standardised on iron ore of about one-half per cent. manganese content.

For manganese ores the procedure is the same up to the removal of the free acid and the addition of zinc oxide emulsion, when the solution is diluted to the mark in a 500 c.c. volumetric flask and mixed. Then 50 c.c. are transferred to a flask, diluted to about 250 c.c., heated to boiling and titrated as before. No zinc oxide emulsion need be added here, the voluminous precipitate of manganese dioxide acting as coagulent.

Strength of Permanganate Solution for Manganese Ores.—One c.c. equals 0·3 per cent. manganese, standardised on manganese ore of known manganese content.

MANGANESE.

Color Comparison on Titration Method.

One gram of the sample in a porcelain dish, or beaker, is warmed after the addition of 25 c.c. of strong hydrochloric and 5 c.c. of strong sulphuric acids, and when in solution the heating is continued until fumes of sulphuric acid appear. The solution is allowed to cool, 25 c.c. of water are added, heat is applied until the salts are dissolved and the solution is transferred to a 50 c.c. volumetric flask, diluted to the mark and mixed. If the color com-

parison method is to be used, the solution should be poured through a dry filler after mixing; if the titration method is to be used, the filtration may be omitted. With a pipette 10 c.c., equal to 0·2 gram of the ore, are transferred into a 1-in. by 8-in. test tube if for comparison, or into a 150 c.c. Erlenmeyer flask if to be titrated. Fifteen c.c. of the nitrate of silver solution are added, the solution is heated over a flame or in a water bath, and about one gram of ammonium persulphate is added. The reaction takes place equally well in a nitric or sulphuric acid solution or a mixture of the two. The essential point is the presence of a sufficient amount of silver nitrate. As soon as the formation of the permanganic acid is well under way, the test tube or flask is removed from the source of heat and placed in a cold water bath. This solution may be compared against the colour obtained from an ore or a steel of known manganese content, in the latter case by dissolving 0·2 gram of the steel in 10 c.c. of nitric acid of 1·20 sp. gr., adding 15 c.c. of the silver nitrate solution and the persulphate as above.

If the solution in the 150 c.c. Erlenmeyer flask is to be titrated, it is diluted to about 100 c.c., 7 c.c. of a 0·2 per cent. solution of C. P. sodium chloride are added, and the sodium arsenite solution is run in until the color is just discharged.

If the insoluble residue is suspected of containing manganese, it is filtered off, burned, 2 or 3 drops of sulphuric (1 part acid to 1 part water) and about 5 c.c. of hydrofluoric acids are added and the solution is evaporated until sulphuric acid fumes appear; 5 c.c.

of the same dilute sulphuric acid are added, and the crucible is warmed till the residue is in solution, when it is added to the main solution.

The stock solution of silver nitrate is made in the proportion of 66·66 grams of the salt to the liter. Twenty c.c. of this solution are diluted to one liter for use, each 15 c.c. contains 0·02 gram of silver nitrate.

The sodium arsenite solution is made by boiling 10 grams of arsenious acid until dissolved in an aqueous solution of 30 grams of sodium carbonate and diluting to 1 liter. About 125 c.c. of the stock solution are diluted to 2,000 c.c., and this solution is standardised on steels or ores of known manganese contents so that 1 c.c. equals 0·1 per cent. manganese on a 0·2 gram sample.

MANGANESE.

Peroxide Reduction Method.

One-half to three grams of the sample in a beaker are digested in 20 to 50 c.c. of strong hydrochloric acid. If the insoluble residue is suspected of containing manganese, a few drops of hydrofluoric acid are added, and the solution is evaporated almost to dryness. Manganese free glass must be used if hydrofluoric acid is employed. Seventy-five c.c. of strong nitric acid are added, the solution is boiled until clear, the manganese is precipitated as dioxide by the addition of a slight excess of potassium chlorate, and the boiling is continued for about five minutes. The solution is cooled, diluted to about 300 c.c. with

cold water, and a definite amount of hydrogen peroxide solution is added from a pipette. After the reduction of the dioxide, the excess of hydrogen peroxide is determined by titration with standard potassium permanganate solution. The value of the peroxide solution in terms of permanganate is determined, and from the total volume of peroxide used, less the excess determined by the permanganate titration, the percentage of manganese is calculated.

The relative value of these two solutions is determined as follows :—About 60 c.c. of strong nitric acid are boiled for about five minutes in a beaker, then cooled and diluted to about 300 c.c. To the cold solution a definite amount of the peroxide solution is added and titrated with the standard permanganate.

The hydrogen peroxide solution is made by diluting 1 lb. of hydrogen peroxide to 9,000 c.c., containing 200 c.c. of strong sulphuric acid.

The permanganate solution contains 1·7375 grams per liter, and is standardised against an ore of known manganese content.

LIME.

The filtrate from the persulphate or bromine precipitation of the manganese, after the basic acetate or ammonia separation of the iron and alumina, is heated to boiling in a No. 6 beaker, 10 c.c. of strong ammonia and 5 c.c. of a saturated solution of ammonium oxalate are added, and the heating is continued until the volume of the solution is reduced to about 150 c.c. When the lime is low it is essential that the evapora-

tion be continued to this point to insure complete precipitation. Five c.c. of strong ammonia are now added, and the solution is boiled for about ten minutes. The precipitate is then filtered off, washed with hot water, burned and weighed as calcium oxide. In normal ores when the lime and magnesia are low, only the first few washings are allowed to flow into the filtrate, the object being to keep the filtrate as concentrated as possible for the magnesia determination which follows. The calcium oxide is also liable to be contaminated with a small amount of silica and when extreme accuracy is desired, the ignited and weighed precipitate is dissolved in warm, dilute hydrochloric acid and the solution is evaporated to dryness. The residue is dissolved in dilute hydrochloric acid, the silica is determined and deducted from the previous weight.

If the lime is to be titrated, it is dissolved on the filter in 25 c.c. of hot, dilute sulphuric acid (1 part acid to 4 parts water), the solution is diluted with 150 c.c. of hot water and titrated with permanganate of such strength that 1 c.c. equals about 0·100 per cent. lime.

MAGNESIA.

The filtrate from the calcium oxalate, which should not exceed 200 c.c. in volume, is made slightly acid with strong hydrochloric acid, and 5 c.c. of a 10 per cent. solution of ammonium phosphate are added, then to the cool solution 25 c.c. of strong ammonia, drop by drop, with continuous stirring during the addition. The solution is stirred at intervals for two or three

hours, or continuously on a machine for one hour, and if permissible it is allowed to stand in a cool place over night. The precipitate is filtered off, washed thoroughly with dilute ammonia (1 part ammonia to 4 parts water), ignited at a low temperature until the filter is destroyed, and finally at the highest temperature of the muffle furnace or blast lamp, and weighed as magnesium pyrophosphate containing 36·24 per cent. magnesia.

SULPHUR.

Fusion Method.

One gram of the sample is intimately mixed in a capacious platinum crucible with about ten grams of sulphur free sodium carbonate, and not more than a half gramme of potassium nitrate. The crucible is heated cautiously over a blast lamp until the fusion is quiet, the last few minutes of the fusion being at the highest temperature of the blast. If sulphur bearing gas is used, the contents of the crucible must be protected from the flame gases with a suitable shield. The fusion is completely disintegrated in hot water, to which a few drops of alcohol may be added to reduce and precipitate any manganese present. The solution is filtered and the residue washed with hot water, or preferably with a 1 per cent. solution of sodium carbonate.

To the filtrate, the volume of which is about 150 c.c., there is cautiously added a slight excess of hydrochloric acid. The solution is heated to the boiling point, 5 c.c. of a 10 per cent. solution of barium chloride are added, and the beaker is placed on the

steam bath or hot plate until the precipitate has subsided. The precipitate is then filtered off, washed with hot water till free from chlorides, burned in an open crucible and weighed; 13·73 per cent. of the weight is sulphur.

If the precipitate is suspected of containing silica, which is rarely the case, it can be purified after ignition by adding a drop of sulphuric and 2 or 3 c.c. of hydrofluoric acids, evaporating and igniting as usual.

If sulphur-free sodium peroxide is used for the decomposition of the ore in place of the sodium carbonate and niter, the fusion is made in a nickel crucible with about 5 grams of the peroxide; the remainder of the treatment is the same.

SULPHUR.

Wet Method.

Five to ten grams of the sample in a porcelain dish or beaker, with a watch-glass cover, are dissolved in 50 to 100 c.c. of aqua regia (1 part nitric acid to 9 parts hydrochloric acid), and the solution is evaporated to dryness. The residue is dissolved in 20 to 40 c.c. of strong hydrochloric acid and the solution evaporated until the first appearance of insoluble ferric chloride. This is dissolved by the addition of a slight excess of strong hydrochloric acid, the solution is diluted to about 75 c.c., and filtered into a suitable beaker, the residue being washed with hot water and the least possible amount of dilute hydrochloric acid.

If the insoluble residue is suspected of containing sulphur compounds insoluble in aqua regia, it is fused

with the least possible amount of sodium carbonate and niter, as previously described in the Fusion Method for Sulphur. The fusion is disintegrated in hot water, the solution is filtered, acidified with hydrochloric acid and added to the main filtrate, or the sulphur may be estimated separately.

The filtrate is heated nearly to boiling, and after the addition of 5 c.c. of a 10 per cent. solution of barium chloride it is again evaporated until a film of ferric chloride appears. This is dissolved by the addition of a few drops of strong hydrochloric acid, and, with a wash bottle, a stream of cold water is forced into the solution until its volume is from 175 to 250 c.c. It is then set aside in a cool place over night. The precipitate is filtered off, washed with hot water and dilute hydrochloride acid until free from iron, burned and weighed as usual.

IGNITION LOSS.

One gram of the sample is placed in a platinum crucible with a tightly-fitting cover and ignited at a bright red heat for fifteen minutes. It is then allowed to cool in a desiccator and weighed. This is repeated with five minutes ignition until constant weight is obtained.

MOISTURE.

A portion, or the entire sample reserved for the moisture determination, in either case not less than two kilograms, is transferred to a suitable pan and weighed, dried at 100° C. until constant weight is obtained and the percentage of moisture calculated.

CUSHMAN'S METHOD OF COMPARING THE RELATIVE RATE OF CORROSION OF IRON OR STEEL SPECIMENS.

In the masterly paper on "The Preservation of Iron and Steel," presented by Dr. Allerton S. Cushman to the meeting of the Iron and Steel Institute held in London in May 1909, the author points out that "the corrosion of iron, like that of other metals, is an electro-chemical phenomenon," and "that in studying iron and steel from the standpoint of their stability, under the conditions of service, we are not dealing with homogeneous, pure metal." Further, he alludes to the fact that "the corrosion of iron does not take place evenly and uniformly over the surface, but that, on the contrary, it is a matter of common observation that iron corrodes rapidly at certain weak points, the effect produced being known as pitting."

Dr. Cushman illustrates the progress of the reaction in ferroxyl mounts in the following manner :—"A $1\frac{1}{2}$ per cent. solution of agar-agar is first made by dissolving a weighed quantity of powdered agar in the requisite amount of water. This solution is boiled for one hour, fresh water being added to replace that lost by evaporation. It is then filtered while hot, and 2 cubic centimetres of standard phenolphthalein indicator added to every 100 cubic centimetres solution, after which it is brought to a perfectly neutral condition by titration with a tenth normal solution of potassium hydroxide (KOH) or hydrochloric acid (HCl), as the case may be. The addition of 7 cubic centimetres of a 1 per cent. solution of potassium ferricyanide to every 100 cubic centimetres of solution

is then made, and the ferroxyl reagent while still hot is ready to use. Enough of the reagent should be poured into a Petri dish just to cover the bottom and the dish floated in cold water until the agar has jellied. A clean sample of iron or steel is then placed on this bed of jelly and covered with the hot solution. After the final addition of agar the dish should not be moved until thoroughly cool. . . . The mounts may be preserved for many months by keeping the surface of the agar covered with alcohol."

"If iron goes into solution, ferrous ions must appear, which, with ferricyanide, form the well-known Turnbull's blue compound." . . . "The pink colour of the indicator is a proof of the presence of hydroxyl ions, and thus indicates the negative poles," as the appearance of the blue colour marks the positive poles. "Some specimens of steel exhibit this phenomena much more quickly and distinctly than others. . . . While the colours sometimes show up immediately, they usually require from twelve to twenty-four hours to attain their most perfect development."

The "auto-electrolysis," which takes place when iron rusts, "should not be confused with the rapid destruction of steel in the neighbourhood of vagabond currents from high potential circuits used for electric lighting or tramways."

INDEX.